W72-07952

PB 208 965

WATER POLLUTION CONTROL RESEARCH SERIES • [illegible]

The Chemical Investigation of Recent Lake Sediments from Wisconsin Lakes and Their Interpretation

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151

U.S. ENVIRONMENTAL PROTECTION AGENCY

292

WATER POLLUTION CONTROL RESEARCH SERIES

The Water Pollution Control Research Series describes the results and progress in the control and abatement of pollution in our Nation's waters. They provide a central source of information on the research, development and demonstration activities in the Environmental Protection Agency, through inhouse research and grants and contracts with Federal, State, and local agencies, research institutions, and industrial organizations.

Inquiries pertaining to Water Pollution Control Research reports should be directed to the Chief, Publications Branch (Water), Research Information Division, R&M, Environmental Protection Agency, Washington, D.C. 20460.

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

1. Report No.

2.

3. Accession No. W 72-07952

4. Title THE CHEMICAL INVESTIGATION OF RECENT LAKE SEDIMENTS FROM WISCONSIN LAKES AND THEIR INTERPRETATION,

5. Report Date

6.

7. Author(s)
Bortleson, Gilbert C

8. Performing Organization Report No.

9. Organization
Wisconsin Univ, Madison[redacted]

10. Project No. EPA Program #16010 EHR 03/71

11. Contract/Grant No.

12. Sponsoring Organization

13. Type of Report and Period Covered

15. Supplementary Notes
Environmental Protection Agency, Water Pollution Control Research Series [redacted] March 1971. 278 p. 35 fig, 36 tab, 198 ref, 2 append[redacted]

16. Abstract

To trace the effects of cultural eutrophication, one meter sediment cores were used to determine the history of calcareous and noncalcareous Wisconsin lakes. Cores were analyzed for carbon, phosphorus, calcium, magnesium, potassium, aluminum, iron, and manganese. Determinations of organic nitrogen, exchangeable ammonium and acid soluble phosphorus were made on selected sedimentary profiles. Recent sedimentation rates and identification of pre- and postcultural sediments were determined by ragweed pollen. Enrichment of phosphorus in postcultural Lake Mendota, Wisconsin, sediments is not only the effect of increased phosphorus supply from domestic sewage, but also due to increase in phosphorus retentive capacity of postcultural sediment and increase of phosphorus deposition due to concomitant increase of iron, manganese, potassium, and aluminum-containing compounds. Evidence indicates long, stable, conditions existed in this lake and watershed prior to human habitation, when phosphorus deposition rate multiplied 5-8 times over the precultural interval. Phosphorus concentration is largely controlled by iron and to a lesser extent by manganese deposition. Chemical stratigraphy of concentration-depth diagrams permits a qualitative evaluation of cultural activities. Potentialities and limitations of using recent lake sediments to evaluate eutrophication are discussed. (Auen-Wisconsin)

17a. Descriptors *Sediments, *Lakes, *Chemical analysis, Stratigraphy, Cores, Lake soils, Evaluation, Sedimentary petrology, Wisconsin, Eutrophication, Chemical stratification, Nutrients, Inorganic compounds, Nitrogen, Phosphorus, Carbon, Calcium, Magnesium, Potassium, Aluminum, Iron, Manganese

17b. Identifiers *Calcareous lakes, *Noncalcareous lakes, Lake Mendota (Wis), Madison lakes (Wis), Post cultural lake sediments, Precultural lake sediments, Organic carbon

17c. COWRR Field & Group 05C, 02H, 02K

SuD EP2.10:16010HRO3/71 $2.25
PB-208 965 MF.95

18. Availability

19. Security Class. (Report)

20. Security Class. (Page)

21. No. of Pages

22. Price

Send To:
WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

Abstractor V. S. Auen va **Institution** Wisconsin Univ, Madison

WRSIC 102 (REV. JUNE 1971)

GPO 913.261

THE CHEMICAL INVESTIGATION OF RECENT LAKE SEDIMENTS FROM WISCONSIN LAKES AND THEIR INTERPRETATION

By

Gilbert Carl Bartleson
University of Wisconsin
Madison, Wisconsin 53706

for the

Environmental Protection Agency

Program #16010 EHR

March 1971

EPA Review Notice

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 20402 - Price $2.25

Abstract

CHEMICAL INVESTIGATION OF RECENT LAKE SEDIMENTS FROM WISCONSIN LAKES AND THEIR INTERPRETATION

Gilbert C. Bortleson

Under the Supervision of Professor G. Fred Lee

In most instances cultural eutrophication is an accomplished fact because there are no data to document what a lake was like in precultural times. The information needed to trace changing limnological and watershed conditions in a lake must come from a record preserved in lake sediments. The chemical composition of 1 m sediment cores fractionated into 5 cm intervals was used to trace the recent developmental history of Lakes Mendota, Monona and Wingra (calcareous lakes in Dane Co., Wis.); Devils Lake (a noncalcareous lake in Sauk Co., Wis.); Little St. Germain Lake, Trout Lake, Lake Minocqua, Weber Lake and Little John Lake (noncalcareous lakes in Vilas and Oneida Co., Wis.). The sediment cores were analyzed for C, P, Ca, Mg, K, Al, Fe and Mn. Organic C and carbonate C were determined separately. Organic N, exchangeable ammonium and acid soluble P determinations were performed on selected sedimentary profiles. Ambrosia (ragweed) pollen was used to establish recent sedimentation rates and to identify pre- and postcultural sediment in the core column.

Changes in the chemical stratigraphy of lake sediment cores are traced to cultural activities in the watershed; these stratigraphic changes are especially pronounced in the southern calcareous lakes. The enrichment of P in the postcultural sediments of Lake Mendota is due not only to an increase in supply of P from domestic drainage, but to an

increase in P retentive capacity of the postcultural sediment and to an increase of P deposition due to the concomitant increase in Fe, Mn, K and Al-containing compounds. The chemical stratigraphy of a 9.9 m Lake Mendota core provided evidence that a long period of stable conditions existed in the lake and watershed prior to the settlement period in southern Wisconsin; the concentrations of organic C, P, Fe, Mn, Al, K, Ca and ragweed pollen are all relatively constant over the interval 62 to 990 cm. The estimated postcultural deposition rate of P (11.9 mg P/cm^2/100 yr) in the center of Lake Mendota is 5-8 times greater than the precultural interval.

A trend which is common to all the northern Wisconsin noncalcareous lakes is an increase in organic C concentration with depth of sediment. The organic C concentration often shows an upward decrease before the postcultural period is initiated; this is followed by a rapid decline in organic C during the postcultural period. The decrease in organic C is usually accompanied by an increase in P, Fe, Mn and/or Al, K, Mg, Ca-containing compounds. The P, Fe and Mn concentration profiles are closely related in both the pre- and postcultural deposits. The concentration of P in the sediments is largely controlled by Fe and to a lesser extent Mn deposition. In general, the aerobic sorption and desorption of P studies indicate the sediment laid down postculturally is a more favorable sorptive environment for P and a less favorable desorptive environment for P than sediment laid down prior to cultural influences. This is due primarily to the concurrent increase in Fe in the postcultural sediments for both calcareous and noncalcareous lakes.

Only in the special case of rate constant sediment accumulation can a rate expression be derived to estimate accurately an incremental change in nutrients to the lake basin. The chemical stratigraphy of concentration-depth diagrams do, however, permit a qualitative evaluation of the extent lakes have been influenced by man's activities. The potentialities and limitations of using recent lake sediments to evaluate cultural eutrophication of lakes are discussed.

APPROVED FOR PUBLICATION

G. Fred Lee
Professor of Water Chemistry

GRADUATE SCHOOL
JUL 20 1970

ACKNOWLEDGEMENTS

My appreciation is extended to several members of the Water Chemistry program who have helped collect core and sediment samples. Special gratitude is due to Professor G. Fred Lee for his advice and assistance throughout this study; my wife Marlene, for encouragement, patience and typing of the manuscript; J. Peterson and J. Delfino, for exchange of analytical results and frequent assistance on sampling trips; R. Plumb for frequent assistance on sampling trips; I. Sanchez for Cu data on Monona core; R. Peters for technical lab assistance; Dr. G. Hanson of the Wisconsin Geological and Natural Survey and Prof. D. Clark of the Univ. of Wis. Geology Dept. for core L-73 from Little St. Germain.

This investigation was supported by the University of Wisconsin Water Resources Center OWRR Project No. A-001-Wis., Training Grant No. 5T1-WP-22 from FWQA and a Research Grant from Wisconsin Water Resources Center - FWQA. In addition, support was given to this project from the office of Naval Research, University of Wisconsin Department of Civil Engineering and Engineering Experiment Station.

TABLE OF CONTENTS

page

Acknowledgements i

List of Figures iv

List of Tables vi

Chapter I Introduction 1

Chapter II Literature Review 3

- A. Natural Changes in Lakes 3
- B. Cultural Eutrophication 6
- C. Stratigraphic Distribution of Possible Indicators of Eutrophication 8
- D. Sedimentation Rate in Relation to a Depth-Time Scale in Lake Deposits 18
- E. Sedimentation Intensity 22
- F. Mixing of Sediments 23
- G. Changes in Lake Sediments After Deposition 26
- H. Sediment Properties Affecting Retention and Release of Phosphorus 29
- I. Other Wisconsin Lake Sediment Studies 40
- J. Summary 41

Chapter III Experimental Procedures 43

- A. Natural Environment 43
- B. Field Sampling Methods 53
- C. Analytical Procedures and Apparatus 54
- D. Statistical Evaluation of Analysis 72

Chapter IV Experimental Results 74

- A. Identification of Pre- and Postcultural Sediments Using *Ambrosia* Pollen 74

B. Chemical Stratigraphy in Calcareous Lakes in Southern Wisconsin 80

C. Chemical Stratigraphy of Noncalcareous Northern Wisconsin Lakes and Devils Lake in Southern Wisconsin 116

D. Estimation of Sedimentation Rates Using Ambrosia Pollen 147

E. Postcultural Sedimentation Intensity 152

F. Sorption and Desorption of Added Inorganic Phosphorus to Pre- and Postcultural Sediments 159

G. Aerobic Leaching of Nitrogen and Phosphorus from Lake Mendota Pre- and Postcultural Sediment 167

Chapter V Discussion....................................... 172

A. Distribution of Carbon 172

B. Distribution of Nitrogen 183

C. Distribution of Phosphorus 192

D. Distribution of Iron and Manganese 212

E. Distribution of Aluminum, Potassium Magnesium and Calcium 222

Chapter VI Evaluation of the Relationship Between the Chemical Composition of Lake Sediment Cores and Lake Eutrophication and Suggestions for Further Research 226

A. Potentialities and Limitations of Using Lake Sediment Cores to Evaluate Eutrophication of Lakes 226

B. Guidelines for Future Lake Sediment Coring Studies 239

Chapter VII Summary 243

Literature Cited 246

Appendix A Chemical Data on Lake Sediment Cores 260

Appendix B Mathematical Formulae Utilized During Investigation 278

LIST OF FIGURES

Figure Page

2.1 Distribution of Carbon, Chlorophyll and Sulfur with Depth of Sediment for Esthwaite and Ennerdale Water (after Gorham, 1961) 14

2.2 Hypothetical Comparison of Phosphorus Sedimentation Intensity Calculated from the Phosphorus Concentration and Rate of Accumulation of the Sediment Matrix 24

3.1 State of Wisconsin Showing General Location of Lakes Studied 44

3.2 Bathmetry and Coring Locations of Lake Mendota 47

3.3 Bathmetry and Coring Locations for Lake Monona 48

3.4 Bathmetry for Trout Lake and Coring Locations for Trout and other Vilas County Lakes 50

3.5 Bathmetry and Coring Locations for Lake Minocqua 51

3.6 Bathmetry and Coring Locations for Little St. Germain 52

3.7 Apparent P vs. Acidity at Different P Concentrations Using Vanadomolybdophosphoric Yellow Color Method 59

4.1 Percent Solids (Dry Weight) with Depth of Sediment in Lake Mendota Cores 84

4.2 Phosphorus Stratigraphy of Deep-water Lake Mendota Cores Fractionated into 5 cm Intervals 86

4.3 Phosphorus Stratigraphy of Deep-Water Lake Mendota Cores Fractionated into 2 cm Intervals and 8 cm Intervals 87

4.4 Chemical Stratigraphy of Lake Mendota Profile WC-89 91

4.5 Chemical Stratigraphy of Lake Mendota Profile WC-86, University Bay 95

4.6 Chemical Stratigraphy of Lake Mendota Profile WC-84, University Bay 96

4.7 Chemical Stratigraphy of Lake Mendota Profile WC-82, University Bay 97

4.8 Chemical Stratigraphy of Lake Mendota Profile WC-92 101

4.9 Chemical Stratigraphy of Lake Monona Profile WC-101 104

Figure Page

4.10 Chemical Stratigraphy of Lake Monona Profile WC-46 106

4.11 Chemical Stratigraphy of Lake Wingra Profile WC-92 109

4.12 Chemical Stratigraphy of Little St. Germain Profile WC-92, West Bay 117

4.13 Chemical Stratigraphy of Little St. Germain Profile WC-56, South Bay 120

4.14 Chemical Stratigraphy of Little St. Germain Profile L-73, South Bay 123

4.15 Chemical Stratigraphy of Trout Lake Profile WC-59, South Bay 126

4.16 Chemical Stratigraphy of Trout Lake Profile WC-60, North Bay 128

4.17 Chemical Stratigraphy of Lake Minocqua Profile WC-51, Northwest Bay 130

4.18 Chemical Stratigraphy of Lake Minocqua Profile WC-52, Southwest Bay 132

4.19 Chemical Stratigraphy of Weber Lake Profile WC-66 135

4.20 Chemical Stratigraphy of Little John Lake Profile WC-67 . 137

4.21 Chemical Stratigraphy of Devils Lake Profile WC-75 140

4.22 Organic Carbon and Ragweed Pollen Profiles for Sparkling Lake Core WC-65 142

4.23 The Effect of pH on the Phosphorus Sorptive Capacity for a Lake Mendota Sediment 162

4.24 Aerobic Release of Inorganic Nitrogen and Soluble Phosphorus from Lake Mendota Precultural Sediment 168

4.25 Aerobic Release of Inorganic Nitrogen and Soluble Phosphorus from Lake Mendota Postcultural Sediment 169

5.1 Phosphorus Concentration and Sedimentation Intensity in Gyttja and Marl Sediments of University Bay and the Deepwater Area of Lake Mendota 200

LIST OF TABLES

Table | Page

3.1 Some Limnologic, Hydrologic and Morphometric Characteristics of Study Lakes 45

3.2 Concentration of Carbon Observed in Sediment Using Peak Height and Clock Integrator Methods 56

3.3 Comparison of Carbonate Carbon Determinations on Lake Mendota Core WC-86 63

3.4 Carbon Recovery of $CaCO_3$ and Glucose After Low Temperature Ashing 65

3.5 Precision of Carbonate Carbon Determinations on Lake Mendota WC-86 66

3.6 Mean, Standard Deviation and Relative Standard Error for Chemical Analysis of a Calcareous and Noncalcareous Lakes . 71

4.1 *Ambrosia* Pollen with Sediment Depth for Noncalcareous Wisconsin Lakes 76

4.2 *Ambrosia* Pollen with Sediment Depth for Calcareous Wisconsin Lakes 77

4.3 Lake Mendota Surface Sediment Data 81

4.4 Statistical Correlation Data for Relationship between Depth of Sample Recovery and Element Concentration in Lake Mendota 82

4.5 The Mean Concentration of Phosphorus in Pre- and Postcultural Lake Mendota Sediment 98

4.6 Mean Concentrations of Pre- and Postcultural Sedimentary Components for Calcareous Lakes 112

4.7 Comparison of Mean Concentration of Postcultural over Precultural Sedimentary Components in Calcareous Lakes 114

4.8 Mean Concentrations of Pre- and Postcultural Sedimentary Components for Noncalcareous Lakes 143

4.9 Comparison of Mean Concentration of Postcultural over Precultural Sedimentary Components in Noncalcareous Lakes.... 144

4.10 Estimated Sedimentation Rate in Lake Deposits Based on *Ambrosia* Pollen Rise 148

Table Page

4.11 Ragweed Counts in Sediment Matrix as a Relative Measure of Sedimentation Rate in Pre- and Postcultural Sediment of Noncalcareous Lakes 150

4.12 Sedimentation Intensity of Postcultural Sedimentary Components for Calcareous Lakes 153

4.13 Calculation of Sedimentation Intensity of Phosphorus for Lake Mendota Core WC-89 154

4.14 Sedimentation Intensity of Postcultural Sedimentary Components for Noncalcareous Lakes 156

4.15 Dry Sediment Accumulation below one Square Centimeter of Mud Surface Since the Onset of the Postcultural Period . 158

4.16 Sorption and Desorption of Added Inorganic Phosphorus to Pre- and Postcultural Sediments of Calcareous Lakes, Woodland and Cultivated Soil in Lake Mendota Watershed . 160

4.17 Chemical Characteristics of Lake Mendota Watershed Soils 163

4.18 Sorption and Desorption of Added Inorganic Phosphorus to Pre- and Postcultural Sediments of Noncalcareous Lakes 165

4.19 Chemical Characteristics of Lake Mendota Pre- and Postcultural Sediments Used in Aerobic Leaching Study 167

5.1 Organic Carbon to Organic Nitrogen Weight Ratio for Lakes Mendota, Wingra and Trout Cores 184

5.2 Exchangeable Ammonium Concentrations in the Pre- and Postcultural Sediments of Lakes Mendota, Monona, Wingra and Trout 187

5.3 Inorganic Nitrogen ($NO_3^- + NH_3 + NO_2^-$ - N) Released from Lake Mendota Pre and Postcultural Sediments 189

5.4 Dissolved Inorganic Phosphorus Released from Lake Mendota Pre- and Postcultural Sediments 199

5.5 Relationship Between Phosphorus, Iron and Manganese Sedimentation Intensity in Noncalcareous Lakes 205

5.6 Comparison of Phosphorus Retentive Capacity and Chemical Characteristics of Noncalcareous Pre- and Postcultural Sediments 206

5.7 Iron to Phosphorus Ratio of the Noncalcareous Pre- and Postcultural Sediments 210

Table Page

5.8 Mean Iron: Manganese Weight Ratio for the Pre- and Postcultural Sediments of Calcareous Lakes 214

5.9 Mean Iron: Manganese Weight Ratio for the Pre- and Postcultural Sediments of Noncalcareous Lakes 219

5.10 Sedimentation Intensity of Aluminum, Magnesium, Potassium and Calcium in Noncalcareous Lakes in Northern Wisconsin.. 223

6.1 Average Percent Increase in Phosphorus Deposition in Little John and Northwest Bay of Minocqua................ 233

CHAPTER I

INTRODUCTION

In most instances cultural eutrophication is an accomplished fact because there are no data to document what a lake was like in precultural times. The information needed to trace changing limnological and watershed conditions in a lake must come from the record preserved in lake sediments. Although several chemical studies have been performed on postglacial sediments and interpreted on the basis of long-term trends, few investigators have given sustained study to the most recent changes in a lake's history. The chemical composition of 1 m sediment cores fractionated into 5 cm intervals was used to trace the recent developmental history of Lake Mendota, Lake Monona, Lake Wingra (calcareous lakes in Dane Co., Wis.); Devils Lake (a noncalcareous lake in Sauk Co., Wis.) and Little St. Germain Lake, Trout Lake, Lake Minocqua, Weber Lake, Little John Lake (noncalcareous lakes in Vilas and Oneida Co., Wis.). The calcareous lakes in southern Wisconsin are eutrophic and the noncalcareous lakes in northern Wisconsin differ in their present-day productivity status and patterns of cultural influence. By comparing and contrasting the core profiles from the same geologic and geographic regions, certain conclusions can be made concerning chemical sedimentation in lakes, particularly in regard to the effects man and his civilization have had on the lakes and recent lake deposits. Lake Mendota was the principal study environment and served as the primary source of information.

If the lake sediments are considered as a part of the dynamic trophic system, then it is worthwhile to consider not merely the reserve of nutrients in the sediments, but also how the change in the chemistry of the sediments brought about by cultural activities has affected the potential for release or retention of nutrients. The dynamic aspects of nutrient enrichment of lakes (eutrophication) will continue into the future, but the rates, dates and relative changes that have occurred as a result of man's intervention will remain speculative until more data are collected about the past chemical history of lakes. Frey (1969) stated at the 1967 Eutrophication Symposium:

> "There is really no need to apologize for the amount of information in sediments; it is tremendous, although still largely unappreciated. Some lines of investigation are already quite highly developed and are yielding exciting results. Others are barely perceived, much less explored. To a considerable extent, it is not yet fashionable to study recent sediments. However, even the relatively few studies that have been conducted make it clear that paleolimnology will have a real impact on our eventual over-all understanding of eutrophication and its effects on lake ecosystems."

CHAPTER II

LITERATURE REVIEW

The change in biota and physicochemical conditions in many of the world's lakes has been attributed to eutrophication. Of major concern is the rate of eutrophication or the rate of change in the manifestations of nutrient enrichment. There are no well defined units or quantitative measures of trophic state. The trophic state of a lake is usually defined by a variety of physical, chemical and biological indicators. For example, some commonly used chemical indicators are sediment type, O_2 deficit, dissolved solids, nutrient concentrations at spring maximum and chlorophyll level.

Limnologists have long recognized that lake productivity is affected by factors other than the concentration of nutrients in a body of water. Rawson (1939) suggested many interrelationships among factors affecting the trophic status of a lake. The nutrient and mineral load imposed on a lake is a function of the geochemistry of its drainage basin, the hydrology of the region, climate and other natural conditions. Superimposed on these natural factors are a variety of human effects, e.g., urban and agricultural runoff and the amount of domestic sewage disposed into the lake. Other factors influence lake productivity primarily by affecting the distribution, availability and the utilization of nutrients. Such modifying factors include mean depth, littoral area, bottom conformation, insolation, temperature, circulation and shoreline irregularity.

A. Natural Changes in Lakes

As a lake ages, it goes through a succession of biological, physical and chemical conditions and events. Most of the lakes in North Temperate regions were formed by glacial action during the Pleistocene, roughly 10,000 - 12,000 years ago. In districts such as northern Wisconsin, where many lakes were originally formed a good many of the small ones have filled in completely and now consist of land occupied by terrestrial vegetation. Under natural conditions lakes proceed toward geological extinction at varying rates of eutrophication or bog formation (Hasler, 1969). Hutchinson (1941) states that three district factors are involved in lake eutrophication: (1) the edaphic factor, representing the potential nutrient supply in the surrounding drainage basin; (2) the age of the lake at any stage, indicating the degree of utilization of the nutrient supply; and (3) the morphometric character at any stage, dependent on both the original morphometry of the lake basin and the age of the lake, presumably influencing the oxygen concentration. Hutchinson maintains true eutrophication takes place only in regions well supplied with nutrients. The many points of view on the question of natural eutrophication and the trophic-dynamic aspect in succession are discussed by Lindeman (1942).

The developmental history of lakes can be called ageing, but all ageing cannot be called eutrophication. Beeton (1966) and Brezonik et al. (1969) proposed several possible lines of change for new lakes formed from glacial origin. The classical scheme of lakes inevitably passing through the evolutionary series of oligotrophy-mesotrophy-eutrophy has been questioned by several recent studies (Goulden, 1964; Mackereth, 1965). Mackereth (1965) theorized that lakes may be more productive in their earlier stages (shortly after glaciation in this case) than later ones.

On the basis of sediment core analyses in the English lake district, Mackereth proposed that these lakes proceed from a eutrophic origin toward an oligotrophic state unless other natural or human disturbance alters their course. Lindeman (1942) and Hutchinson and Wollack (1940) also suggested the initial period of oligotrophy is relatively short after glacial scour. Lindeman (1942) considered the early eutrophication period to level off and a long period of relatively constant production to ensue in a lake. This stable period is termed stage-equilibrium, during which the sediments act as a nutrient reservoir or trophic buffer to maintain high production. During the stage-equilibrium, sediments continue to accumulate and the lake approaches extinction. It may be instructive to recognize Lindeman's senescent stage as another major lake class. This would represent the final evolutionary stage of a lake and would have the characteristics described by Lindeman: shallowness, large littoral area, high standing crop of macrophytes and low production per unit area. The supposed irreversibility of eutrophication was questioned by Cowgill and Hutchinson (1964), who reported a case of apparently reversible eutrophication during the time of the Roman Empire. Lag Monterosi rapidly became eutrophic when the Roman road was built around the lake and later became oligotrophic. The eutrophic period in the lake's history was recognized by the kinds of diatoms found in the cores.

In summary, then, the following factors became major determinants in the rate of development of the trophic character of the lake: geology of the region, size and configuration of the lake basin, type and size of watershed and latitude of the lake's location. It has not yet been possible to estimate accurately the basic natural rate of eutrophication and the position of natural eutrophication in a lake's evolution.

B. Cultural Eutrophication

The influence of man in the lake's watershed can result in an increased rate of nutrient influx to the lake which will bring about an accelerated rate of undesirable chemical, physical and biological effects. This process of lake fertilization has often been distinguished from natural eutrophication. There is a general agreement among present workers that cultural eutrophication is nutrient enrichment, but many differences in opinion exist concerning details of the process and its effects.

Over the past 50 years it has become clear that large-scale human use of certain lakes has accelerated eutrophication. Most of the enrichment of lakes and streams in Switzerland were caused by cultural activities of man, especially the discharge of sewage (Thomas, 1962). In the U.S. similar cultural eutrophication has been noted for the Yahara lake chain in Wisconsin, Lake Washington in Seattle, Lake Erie, Lake Tahoe and others. The reader is referred to Stewart and Rohlich (1967) for case histories of lakes in the world that have recently undergone changes. Many case histories of changing lake conditions reviewed by Stewart and Rohlich (1967) do not concern nutrients directly, but rather other indices which the authors used to interpret changes that take place.

Increases in concentration of dissolved solids and/or certain ions, such as chloride, have been observed in several lakes including the Great Lakes (Beeton, 1965, 1966). Beeton (1966) suggested that these changes might more appropriately be called environmental changes, which might not indicate eutrophication. Nevertheless, Beeton explained they are due to man's use of the environment, and increases in the major ions probably reflect what is happening to the nutrients.

Somewhat more controlled are situations in which lakes have been fertilized deliberately with quantities of nutrients to increase productivity. For example, enough inorganic fertilizer was added to Bare Lake, Alaska, to give 25 ppb P in the form of phosphate and five times the amount of N in the form of nitrate (Nelson and Edmondson, 1955). Fertilization was followed by a very great increase in the growth of algae. According to Edmondson (1968), as far as experience goes, most lakes appear responsive to fertilization most of the time. Edmondson (1968) also recognized that because of the interaction of environmental factors and the influence of size, shape, depth, exposure to wind, and rate of replenishment of water on the ability of a lake to produce a crop of organisms with a given supply of nutrients, different lakes will have different sensitivity to enrichment. Ohle (1955, as cited by Stewart and Rohlich, 1967) felt that the increased inflow of nutrients into an oligotrophic lake was not as noticeable as it was in the eutrophic lakes of northern Germany. However, Ambühl (1962, as cited by Stewart and Rohlich, 1967) regarded oligotrophic lakes as the most sensitive to increases in nutrients. Brezonik et al. (1969) studied the artificial eutrophication of a small Florida lake by imposing a nutrient load at a controlled rate. A lake with similar characteristics about 1/2 mi from the one receiving the nutrient input served as the control. Brezonik et al. (1969) concluded that qualitative classification based on chemical and biological information was possible. However, the quantitative classification was impossible since more than one criterion is required to define trophic state and because the relationships among the various criteria remain undefined.

It would appear from the case histories of culturally eutrophic lakes and the deliberate fertilization of lakes that increased input of nutrients often causes measurable changes in biota and physicochemical conditions. But, indicators of trophic state are only qualitative; it is yet impossible to state specifically how much more eutrophic one lake is than another or to express the rate of cultural eutrophication of a lake, when using certain criteria of trophic status.

C. Stratigraphic Distribution of Possible Indicators of Eutrophication

Biological Indicators. Biologists have long favored the use of indicator organisms to detect changes in trophic state. Increases in the abundance and changes in species composition of plankton and zooplankton have been proposed as indicators of trophic state. Frey (1969) states that lakes are sensitively responsive to any changes that affect their water, energy and nutrient budgets. Therefore, long-term changes in climate and edaphic conditions, including the phenomenon of eutrophication whether natural or accelerated by man, induce progressive changes in the biota. Virtually all groups of animals occurring in inland waters leave at least some morphological remains in sediments (Frey, 1964). The groups best represented in the sediments are the Cladocera, midges, rhizopod Protozoa, ostracods, Turbellaria, Coleoptera and molluscs (Frey, 1969). Among the algae, the diatoms and some green algae, Chrysophyceae are represented in sediments.

Diatoms have been the plankton form studied most often as an indicator organism because of suitable preservation of siliceous frustules. Kendall (1969) suggested, however, that the dissolution of diatom frustules after death may explain fossil diatom trends for Lake Victoria, East Africa in accordance to pH shifts of the water historically. Analysis of diatoms in sediment cores have been made on a number of well studied lakes. Notable among these are Pennington (1943) on Windermere, Patrick (1943) on Linsley Pond, Nygaard (1953) on Lake Gribsø and Round (1961) on Esthwaite Water. Stockner and Benson (1967) examined the diatom remains in the recent sediment of Lake Washington. In the deeper sediment, which was deposited prior to cultural enrichment, the relative composition of diatoms was constant. Correlated with the pattern of sewage discharge into the lake, many of the species changed in accordance with their ascribed trophic behavior as indicator species. Stockner and Benson cautioned, however, that the indicator species approach to the interpretation of sedimented diatoms leaves much to be desired because of inadequate knowledge of nutritional physiology and of the ecology of freshwater diatoms. Edmondson (1969) noted that many species substitutions will also be effected by competition and predation, and not depend on a simple and direct way on physiological tolerance or nutritional requirements. Round (1964) found from the study of cores in the English lakes that long-term changes in the diatom floras occur in a cyclical sequence. He felt it was best to consider whole assemblage of species and to take into account absence of species. Davis (1964) reviewed Lake Erie phytoplankton data and reported changes from a centric-dominated diatom assemblage in 1880 to one characterized by alternate pulses of araphidinate- and centric-dominated assemblages. Charlton (1969) examined the ecological and sedimentological history of Little St. Germain, Wis. He concluded, based on the Centrales: Pennales diatom ratio and the ecological requirements of the diatom species, that East Bay, nearest the inlet, became eutrophic long before man's influence and that South Bay, nearest the outlet, became eutrophic only in recent times. A 19-inch core was collected from Lake Sebasticook, Maine, and several 1-inch segments of the core were examined to enumerate diatom skeletons (FWPCA, 1966). High diatom counts occurred in the upper 12 inches of deposits, and the authors attributed the change to recent nutrient enrichment of the lake.

Lake sediments contain large numbers of microfossils of various Cladocera zooplankters. Several investigators have suggested that the type or quantity of cladoceran remains in the sediments reflects changes in lake conditions or trophic level of the lake (Deevey, 1942; Goulden, 1964; Frey, 1964; Deevey, 1969; Goulden, 1969). The replacement of Bosmina coregoni (longispina) by B. longirostris in lakes undergoing eutrophication has been observed in Lake Washington (Edmondson et al. 1956) and in sediments of Linsley Pond (Deevey, 1942) and Esthwaite Water (Goulden, 1964). Deevey (1942) found a striking similarity in the shape of the curves representing Bosmina content and total organic matter plotted against depth, which, when plotted logarithmically against each other, showed a linear relationship expressed by an empirical power equation. That is, the growth and differentiation of Bosmina were comparable to the organic content of the sediments. The general sequence of changes in Bosmina numbers followed periods of exponential rise, more or less stable equilibrium and a decline which was probably due to changes within postsettlement times. Vallentyne and Swabey (1955) suggested that the initial rise in productivity and the increase in Bosmina in the early history of Linsley Pond were both dependent on climate. Based on the distribution of Cladocera and midge remains in Esthwaite cores, Goulden (1964) concluded that the lake was oligotrophic for most of its development and only within the last 900 years became eutrophic under the influence of man. Further, Goulden associated each of the four maximum Cladocera horizons with increased productivity due to climatic or cultural changes in the drainage basin. Rather than an unidirectional transition from an oligotrophic to an eutrophic condition, according to Goulden, the midge and Cladocera evidence suggests that the lake alternated between the two tendencies. After the examination of the Madison lakes, Frey (1960) found that the quantities and species of Cladocera remains in the sediments gave some indication of past production of plankton. However, Harmsworth and Whiteside (1968) concluded that the abundance of cladoceran microfossils from cores used to study lake history is not necessarily related to primary productivity and that numbers of remains should not be compared from different lake systems.

The commonest insect remains in lake sediments are those of midges. Stratified harmonic lakes have been classified on the basis of their profundal chironomid fauna into oligotrophic Tanytarsus lakes, mesotrophic Stictochironomus/Sergentia lakes and eutrophic Chironomus lakes (Stahl, 1969). In the profundal benthos, midges that require high oxygen content are replaced by those that can tolerate lower oxygen levels, and they in turn by others that can tolerate still more taxing conditions. The uses of chironomids and other midges in interpreting lake histories has been reviewed by Frey (1964) and Stahl (1969).

Chemical Indicators. The sediments of any basin contain clues to the chemical history of that basin, but the interpretation of the sediment record is often difficult. The chemistry of the sediments is the result of an involved series of precipitation, complexation, exchange and sorption reactions covering a long period of time, between diverse solids and complex solutions, both in the water column and in the sediments below. Nevertheless, investigators have made general inferences about chemical events which have occurred in the historical past. Organic matter in the sediments has often been used as a rough index of past aquatic productivity.

In a comprehensive study on the sediments in the Lake District of England, Mackereth (1966) examined the vertical distribution of Na, K, Ca, Mg, Fe, Mn, S, C, H, N, P. Zn, Cu, Co and Ni. Mackereth felt that the composition of sediments eventually reaching the lake bed could be accounted for in terms of rates of erosion in the drainage basin rather than in terms of the changing rates of organic productivity either on the drainage basin or in the lake waters. He concluded although the gross composition of the sediment is largely dependent on conditions in the drainage system rather than in the lake waters, some deductions can be made which indicate the availability of nutrients dissolved in waters of lakes in past times. If the material is rapidly removed from the drainage basin by erosion, nutrient elements are lost to the sediment locked in the lattice of unleached mineral particles. If, however, the rate of erosive removal of soil from the land surface is reduced, the mineral particles are held in the soil column in a position which allows more efficient leaching of soluble components, which then become available to the populations of the lake.

Gorham (1961) examined the distribution of carbon, chlorophyll derivatives and sulfur in cores from the fertile Esthwaite and unfertile Ennerdale in England. Chlorophyll derivatives, S, and C exhibited similar trends in each of the sediment cores as shown in Figure 2.1. In Esthwaite maximum levels of all three constituents were reached early in the course of lake development, while in Ennerdale maxima were attained much later. In the case of chlorophyll derivatives and S, the concentrations were much lower in Ennerdale than Esthwaite. According to Gorham, the higher levels of S and chlorophyll, and the high ratios to C, were associated with strongly reducing conditions which were more likely to occur in the surface sediments and bottom waters of productive lakes such as Esthwaite than in those of infertile lakes like Ennerdale. In Esthwaite all three constituents showed a rapid rise in profile distribution deep in the mud column implying the lake became eutrophic early in its history; the maximum percentages of C occurred only a little above the glacial clay. In contrast to Esthwaite, maximum concentrations were reached more slowly in Ennerdale and occurred in the upper half of the mud column.

Hutchinson and Wollack (1940) determined Si, Al, Ti, Fe, Mn, Ca, Mg, P, S, N and lignin from 13 levels of a 43 foot profile taken in the sediments below deep water in Linsley Pond. Considerable increase in the inorganic content in the most recent unconsolidated sediment at the top of the profile was taken to indicate recent erosion of cultural origin. Silica and Al were essentially constant, except at the bottom of the core

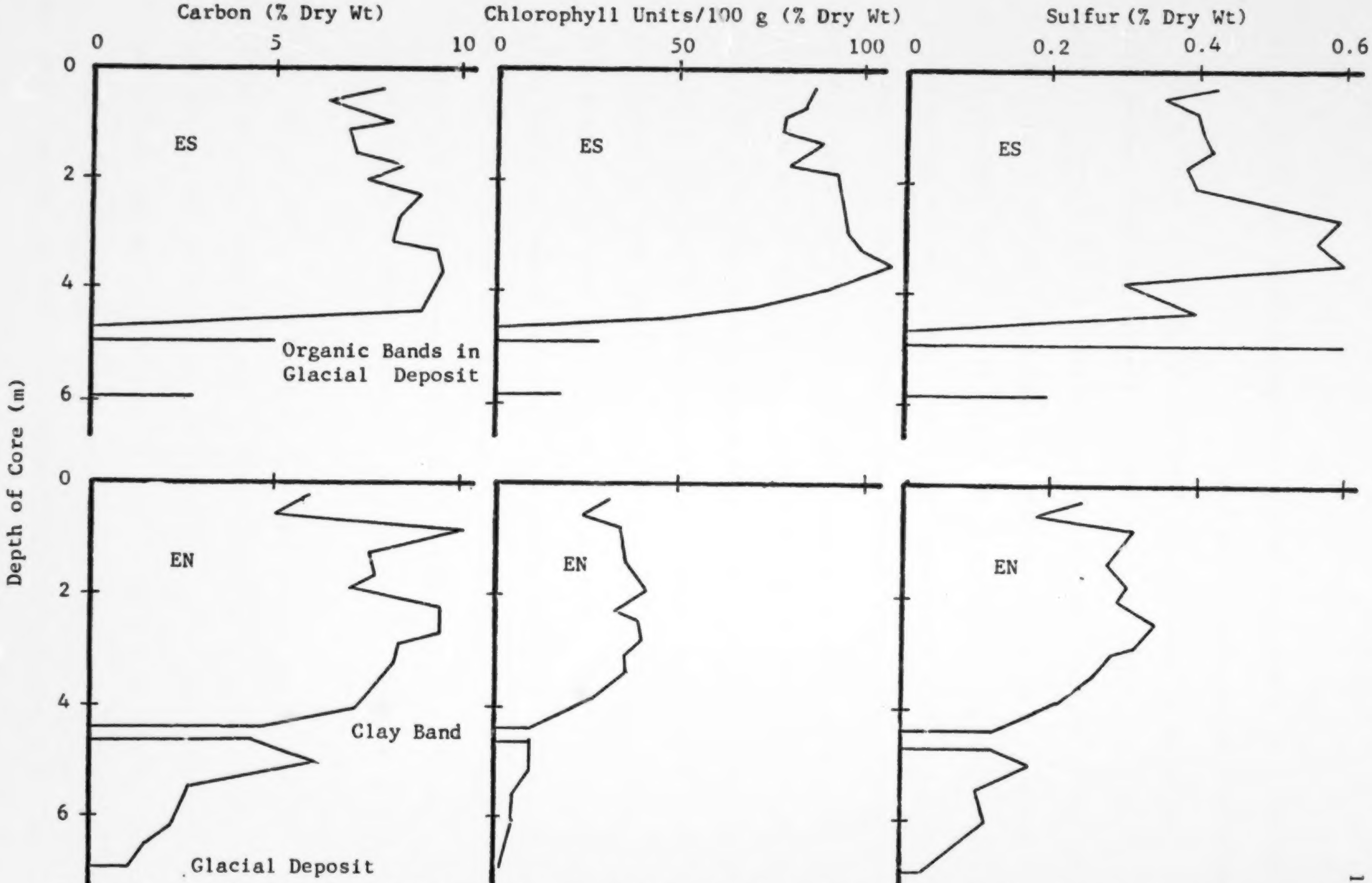


Figure 2.1 Distribution of Carbon, Chlorophyll and Sulfur with Depth of Sediment for Esthwaite Water (ES) and Ennerdale Water (EN) [After Gorham, 1961].

where the sediment was rich in clay from the erosion in the basin in early postglacial time. The distribution of organic matter in the profile was believed by Hutchinson to indicate a rapid change from oligotrophy to eutrophy, followed by a long period of approximate equilibrium in eutrophic conditions.

Horie (1966), on the basis of an upward increase in sedimentary N concentration of Lake Yogo, Japan, concluded that the lake became more eutrophic. Horie felt that the trophic stage might well be controlled by changes in lake level which probably had fluctuated many times by both crustal deformation and oscillations of climate. Apparently the lake had repeated oligotrophic and eutrophic tendencies.

A 286 cm core of sediments was taken from the center of Potato Lake, Arizona, (Whiteside, 1965). Pollen, chemical and physical analyses were made on the sediment. It was assumed that the increase of organic matter above 120 cm in the sediments occurred during eutrophication. The increase in production corresponded to changing climatic conditions as indicated by the pollen diagram. According to Whiteside, the variations of Fe, Mn and Ca could be explained by lake succession from oligotrophic to eutrophic conditions. Within the core two pollen zones were observed: One extending from the surface to 120 cm and the other below this level. The upper pollen zone was dominated by an abundance of pine pollen. Below 120 cm, the most abundant tree species were believed to have accumulated during a period of cool and moist climate different from modern conditions.

In another investigation of lake sediments, Murray (1956), who cored Lake Mendota and Trout Lake extensively, reported evidence for recent increases in clastic material. He determined organic matter, carbonates and clastic material for several stations in each of the lakes. Based on his study, he felt that an important change in the sedimentation of Lake Mendota occurred at some time in the recent past. The new sediment, the black sludge, differed from the older buff marl in having a much higher clastic content and being correspondingly lower in carbonate. The organic content of the marl and sludge was similar. Murray demonstrated in his study that the best explanation for this change was a large increase in clastic deposition with little or no change in the formation of carbonate; the clastic material thus masked the carbonate giving a high clastic - low carbonate sediment. Murray stated the mechanism for producing the sludge required a corresponding increase in organic deposition to maintain a similar level of organic content in both the marl and sludge. The increase in clastic content was attributed to farming in the basin and shoreline development since the mid 19th century.

Several investigators have analyzed plant pigments in lake sediments to provide clues to the history of changing conditions in lakes. An increase in the amount of chlorophyll degradation products or carotenoids in sediment profiles has been considered indicative of a period of greater productivity (Vallentyne, 1955; Fogg and Belcher, 1961). The use of fossil pigments to measure historical productivity has many restrictions. Low pigment concentrations in sediments may not permit distinction between low productivity and rapid diagenesis or, conversely between high productivity and little diagenesis (Brown, 1969). Also, there is no simple relationship between pigment distribution and taxonomic units for identification of paleo-populations (Brown, 1969).

Griffiths et al. (1969) determined oscillaxanthin known to be produced by Oscillatoria rubescens and O. agardhii in cores from Lake Washington. The authors related the vertical distribution of oscillaxanthin within the sediments to the recent history of sewage enrichment of the lake. Vallentyne (1955) has analyzed sediment cores from six lakes for chlorophyll degradation products. Chlorophyll units and ignitable matter followed similar trends in each of the cores. Low chlorophyll was generally found at the bottom of each profile and was followed by a steep rise in concentration to a near maximum level which remained more or less constant throughout the upper sequence. As the carotenoid myxoxanthophyll is restricted in distribution to blue-green algae, Zullig (1960, as cited by Brown, 1969) was able to use its occurrence in lake sediments as a selective indicator of the existence of former populations of this algal. A review is given by Brown (1969) and Vallentyne (1969) on the distribution of fossil pigments in sediment cores.

Increases in concentrations of sedimentary amino acids, carbohydrates and pigments occur from a few centimeters to a meter or more below the surface of many lake and bog sediments (Swain et al. 1964; Rogers, 1965) Swain (1965) concluded from a review of some quaternary lake sediments of North America that residual organic substances in lake and bog sediments show at least a generalized relationship to trophic and climatic history of the body of water. In the case of many organic substances, the problem is complicated by possible postdepositional changes within the lake sediments by microbial synthesis, sorption and other causes.

Relative sequences of events in a lake's trophic history can be elucidated by the stratigraphic observation of chemical and biological indices. Even though the sediments provide a storehouse of information regarding past events, the interpretation of a sedimentary sequence in a lacustrine environment realizes formidable limitations. The following four sections reflect upon several complications arising in the observation of recent sedimentary profiles.

D. Sedimentation Rate in Relation to a Depth-Time Scale in Lake Deposits

Unfortunately, the amount of information that can be extracted from lake sediment core analyses is often limited by the lack of an absolute depth-time scale for the deposits. To interpret the sediments in terms of nutrient income and past conditions of a lake, it is desirable to have some time scale to relate the age of sedimentary events or the rates at which sedimentary deposits were formed. The determinations of the elementary composition of sediments are usually expressed as percentages of the dried sample. Percentage diagrams suffer the deficiency that all changes from one level to another are strictly relative. If numbers per unit volume (or weight) of sediment are plotted against depth, the changes from one level to another are absolute, providing that the rate of sedimentation has remained constant. Over short time intervals this assumption is reasonably valid, but over long time intervals it is not. The ideal is to present the stratigraphy in absolute terms, i.e. $mg/cm^2/yr$.

For sediments within the age range of radiocarbon, a curve showing the rate of sedimentation as a function of time (or depth) can be constructed from a series of C-14 dates within a core. The radiocarbon ages of 24 samples were plotted against their depths below the mud surface to show the relationship between depth and age of sediment, by Davis (1967), for Rogers Lake, Connecticut. A derivative of a second-degree polynomial equation was found that approximated the lower portion of the core, and a first-degree equation was found that approximated the younger sediment. The dating of the Rogers Lake profile allowed Davis to estimate the accumulation rate of pollen types as a variable independent both of changes involving other pollen types, and of change in the rate of accumulation of the sediment matrix. A series of C-14 dates were obtained by Ogden (1967) from core samples from Seth's Pond, a soft-water lake in Massachusetts, and Silver Lake, a hard-water lake in Ohio. A fitted regression curve of the form, $Y_x = cX^a$, was obtained for sample age, X, with sample depth, Y_x, in order to calculate sedimentation rates. In both lakes, the sedimentation rates for postcolonial time (above the sharp rise in Ambrosia and European weed pollen) were considerably greater than they were in the rest of the cores. Ogden discussed the limitations of the radiocarbon technique in estimating the age of sediments because of dilution of atmospheric C-14 by "dead" carbon derived from Paleozoic limestone and the introduction of C-14 into the atmosphere by nuclear testing. The errors in the estimates of sedimentation rate are largely due to uncertainity in the C-14 measurements. One source of uncertainity in C-14 measurements is the well-known possibility of error through the admixture of older carbon in lacustrine materials or through contamination of the sample with foreign carbon. Pennak (1963), on Colorado mountain lakes, and Kendall (1969) on Lake Victoria, East Africa have also determined rates of sedimentation by a series of C-14 dates. Many other workers have determined from a single or a few C-14 measurements a constant or average rate of sedimentation.

Livingstone (1957) considered banded and varved sediments to be of the utmost value in dating sediments. If the annual increment of sediment remained as a discrete layer, one could count these layers, thereby establishing an absolute chronology for the lake. In practice such annual layers can seldom be discerned. A number of instances are known, however, in which annual laminae occur. Vallentyne and Swabey (1955) found a series of brown bands near the bottom of Linsley Pond deposits. The bands probably reflected some event that occurred 2 or 3 times a year, possibly the diatom maxima (Livingstone, 1957). The alternating brown and black bands were used by Livingstone (1957) to determine the Bosmina, organic and inorganic content per cm^2 per year from the 44 to 32 foot level of a Linsley Pond core. Ludlam (1967) found the sediments in the southern half of Cayuga lake were generally banded. The deposition of a couplet of a dark and pale band seemed to be controlled by the annual variation in the supply of allochthonous organic detritus and clastic sediment. There was close agreement between the couplet counts of major bands and the years between 1935 and the dates of floods or periods of high lake level; thus the sediment samples were dated by the couplet counts. In two lakes in southern Ontario (Tippett, 1964), the alternating calcareous and organic members have been shown to represent annual deposits by differential analysis of pollen and diatoms.

Several investigators have determined sedimentation rates by other means than using an indicator to give the age of a stratum. Some of the early methods assumed either a constant or average rate of sedimentation of one component of the core sediment or an average rate of sedimentation for total core material. Toyoda et al. (1968) constructed a time scale for Lake Biwa, Japan based on the assumption that silicon was deposited at a constant rate. Therefore, a change in the silicate concentration in the core was taken to be indicative of a change in sedimentation rate. It is probably dangerous to assume a "constant" rate of sedimentation for any component in the sedimentary column in inferring dates. Charlton (1969) calculated the present day sedimentation rate of Little St. Germain from the annual silica budget of the lake. In estimating the sedimentation rate from the total supply of a sediment component, the investigator assumes that the sediment is settled uniformly over the entire basin. Hutchinson and Wollack (1940) constructed a depth-time scale for Linsley Pond deposits based on a limiting assumption that unit mass of ash was deposited in unit time. This was done by plotting ash content per unit wet volume against depth and integrating planimetrically between the bottom and each depth. The depths were then spaced from the bottom upwards at distances equal to the successive values of the integral.

Several workers have used the recent rise in Ambrosia (ragweed) pollen to calculate recent sedimentation rate since the onset of cultural activities (Davis, 1968; Ogden, 1966; Ogden, 1967; Lewis and McNeely, 1967). Ogden (1967) found that because of the variability of near surface sediments as a result of bomb-produced C-14, limnologists and pollen stratigraphers need some calibration marker other than the present mud/water interface for C-14 dating. He indicated that Ambrosia pollen analysis can be used to establish a boundary, that can be dated for each site from historical records, whose variation in stratigraphic age is less than the usual counting error by C-14 analysis. Also, ragweed pollen provides a time marker for recent sediments which are not in the age range of radiocarbon.

Most lacustrine dating has been done to establish a depth-time scale for pollen or fossil analysis. Sample ages for chemical and biological sedimentary sequences have received little attention. Davis (1967) points out that the results from Rogers Lake indicate that an estimation of sedimentation rates by means of a series of C-14 dates is feasible. But she questions whether such an expensive and laborious method is worthwhile since, when the deposition rate is relatively uniform, the percentage diagram conveys almost all the information about changes as the deposition rate diagram.

E. Sedimentation Intensity

Graphs of sediment age vs. wet sediment thickness may give a misleading picture of deposition rates because compaction, as well as age, increases with depth. In order to compare the rates of accumulation of materials of differing composition, moisture content and compaction, it is more meaningful to give the rate of sedimentation in units of weight per unit of area and time, which can be called sedimentation intensity. If the thickness per year, water content and density of the deposits are known, sedimentation intensity can be calculated. The time represented by a unit of sediment thickness can be estimated by a number of methods, as discussed previously, from various levels within a core of lake sediment. The deposition time for a unit thickness of sediment varies, of course, in different parts of the profile. This fact points to the importance of obtaining a series of dated stratum to reveal changes in accumulation due to core compaction.

The additional information obtained by transforming chemical changes in concentration in a sedimentary profile to sedimentation intensity is demonstrated in Figure 2.2. In sample (1), the P concentration per unit wet volume is five times greater than sample (2); however, the rate of accumulation per cm takes 20 years for sample (1) and four years for sample (2). Thus, the resultant yearly influx (mg $P/cm^2/yr$) for both samples is the same. Often results based on the absolute rate of accumulation can lead to vastly different interpretations than those based on percentage diagrams (Davis and Deevey, 1964).

F. Mixing of Sediments

There are several lines of evidence that mixing in lake sediments is taking place and that the surface sediments are being contaminated by older materials. The extent of mixing, of course, will determine the resolution of the chemical, biological or physical stratigraphy. In other words, does the chemical record show changes of 10 years, 100 years or 500 years for a given interval size? In dealing with long-term trends with intervals spaced 5 cm or more apart, mixing may be advantageous in that the resultant integration of old and recent sediment particles make less necessary any effort to analyze more closely spaced intervals. On the other hand, if the sedimentation rate is slow, the vertical mixing layer deep, the interval small and the investigator interested in short-term trends, the extreme is represented in the seriousness of mixing.

Mixing of sediments is suggested by the simple observation of burrowing organisms and burrows at various depths in the sediment cores.

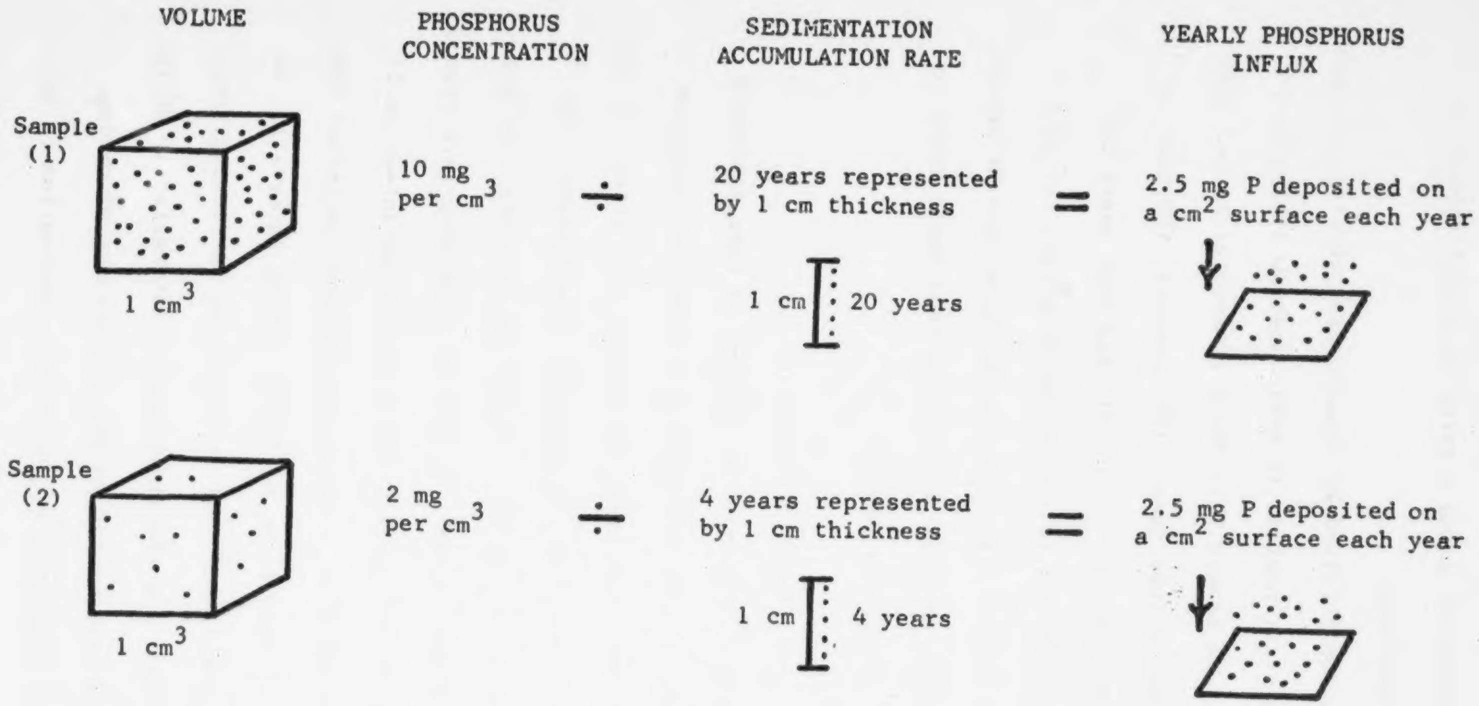

VOLUME
PHOSPHORUS CONCENTRATION
SEDIMENTATION ACCUMULATION RATE
YEARLY PHOSPHORUS INFLUX
Sample (1)
1 cm3
10 mg per cm3
÷
20 years represented by 1 cm thickness
1 cm
20 years
=
2.5 mg P deposited on a cm2 surface each year
Sample (2)
1 cm3
2 mg per cm3
÷
4 years represented by 1 cm thickness
1 cm
4 years
=
2.5 mg P deposited on a cm2 surface each year

Figure 2.2 Hypothetical Comparison of Phosphorus Sedimentation Intensity Calculated from the Phosphorus Concentration and Rate of Accumulation of the Sediment Matrix.

Cole (1953) found from ninety vertical core samples in Douglas Lake, Michigan, that 93 percent of the microbenthic forms were in the uppermost 14 cm, with greatest concentrations in the upper 1-2 cm level. The deepest penetration was the 20-24 cm stratum. Berg (1938, as cited by Cole, 1953) stated that upwards of 90 percent of the macroscopic bottom fauna were between 0-15 cm in several Danish lakes he investigated. However, depth of burrowing was found to vary from lake to lake--the softer the bottom the deeper the burrowing. Kleckner (1967, as cited by Griffith et al., 1969) has shown that the chironomids and tubificids can cause appreciable transport of surface material to a depth of about 3 cm. Vieth (1968) found that toxaphene applied to a lake for rough fish control was mixed downward into the sediments a distance of 10 to 15 cm in nine months. Twenhofel and McKelvey (1941) argued that their inability to detect laminations in Wisconsin lake sediment cores results largely from intensive reworking of them by benthos. The thickness of the homogeneous mixed layer, which is often associated with the oxidized mud zone, probably varies considerably in different lakes. Hayes, Reid and Cameron (1958) presented evidence that the real oxidized layer was only one mm thick or less. Similar results were reported by Zicker et al. (1956). Gorham (1958) reported that the thickness of the oxidized microzone may depend upon the turbulent displacement of the uppermost sediments due to wind currents. The reader is referred to Lee (1969), Ogden (1967) and Davis (1967) for discussion on further evidence of mixing of sediments.

Mathematical mixing models have been proposed by Berger and Heath (1968) and Davis (1967). A simple conceptual model included a homogeneous layer of variable depth below the sediment-water interface where the particles become thoroughly mixed with older deposits, and a historical layer where particles come to rest. The vertical mixing in sediments can be quantitatively described if several assumptions are made. For example, in the models proposed, it is assumed that a particle just deposited can reside with equal probability at any depth within the homogeneous layer. In reality a decreased intensity of mixing with depth below the surface probably occurs.

In the interpretation of the sedimentary record the assumption is generally made that there has been essentially no movement of materials upward or downward except in the biologically active layer near the surface. A given interval size in the core column will contain the integrated chemistry over a time span which is dependent on such factors as sedimentation rate and depth of the mixing layer.

G. Changes in Lake Sediments After Deposition

The changes that can take place after deposition are an important aspect in the interpretation of the chemistry of lake sediment cores. Despite the great importance to the problem little is known about the subject. According to Larsen and Chilingar (1967), diagenesis would include all physical, biochemical and physicochemical processes which modify sediments between deposition and lithification or cementation at low pressures and temperatures. Recent sediments usually reveal only early stages of diagenesis. The earliest diagenetic processes involve consumption of oxygen by organisms below the depositional interface which changes the environment from oxidizing to reducing (Allgeier, et al., 1941; Mortimer, 1941; Armstrong, 1967). The redox potential is particularly affected by the zone of maximum bacterial activity (Zobell, 1946). The extent of the bacterially active zone may be directly related to the rate of sedimentation. Butkevich (1938, as cited by Bordovskiy, 1965) has shown where sediments deposit rapidly, active bacteria occur in deposits of great depth, and where sediments accumulate relatively slowly, active bacterial forms occur only in the uppermost layer of material. According to Krumbein and Garrels (1952) the maximum effect of diagenesis can be expected where fairly rapid deposition takes place under conditions of positive Eh, with the entrapment of abundant organic material. Conversely, the minimum effect should occur in an environment where conditions are strongly reducing at the depositional interface, so that burial produces no real change, and in deposits with little or no organic matter.

Emery and Rittenberg (1952) studied the diagenesis of recent sediments off the southern California coast. Some changes they noted in cores were as follows: (1) the water content markedly decreases with depth of burial and is greatest in the finest sediments, (2) the pH of the sediment surface is slightly higher than that of the bottom water and generally increases with depth of sediment. The zone of lowest pH occurs at a depth of maximum bacterial activity and where sulfates, nitrates and CO_2 are formed by oxidation. Bacterial reduction of sulfates and possibly base exchange give rise to higher pH at depth, (3) the lowering of Eh is due to the withdrawal of dissolved oxygen from the interstitial solutions in the upper layers and to the action of sulfate-reducing bacteria on dissolved sulfates at greater depth, (4) the ammonia content is greatest at depth in the sediment and (5) the organic N and organic C both decrease with depth of sediment. In contrast to the decrease of organic N and organic C with depth of burial noted by Emery and Rittenberg in marine sediments, the organic C and organic N were found to increase with depth of sediment over a one meter interval for Trout Lake, Wis. (Murray, 1956; Bortleson, 1968). The lignin content of the gyttja was determined by Twenhofel et al. (1945) for several cores from Trout Lake. Twenhofel et al. had anticipated that the bacterial decomposition would have led to a decrease in the nonligneous materials and thus an increase of ligneous materials with depth. They concluded that the fact such a decrease was not observed suggested that bacterial activity ceased in the organic sediments of Trout Lake shortly after burial. Hutchinson and Wollack (1940) believed the diagenetic loss of organic matter was strictly limited to the unconsolidated modern mud in Linsley Pond. According to Degens (1967), the early stages of diagenesis involve microbial and chemical (hydrolysis) destruction of biochemical macromolecules. Although the main function of bacteria is the decomposition of organic matter, they also play an important part in its synthesis. A review of the abundance, structural composition and stability during diagenesis of several organic components is given by Degens (1967). Some aspects of changes and transformation of organic matter in bottom marine sediments is presented by Bordovskiy (1965).

Changes after deposition seem to be more or less intimately connected with the work of bacteria and other microorganisms. The bacterial population is richest in the upper film of sediment; the numbers of bacteria are greatly reduced below (Bordovskiy, 1965). The role of anaerobic bacteria increases with depth of sediment. Sediment profile counts of bacteria were made by Henrici and McCoy (1938) for several lakes in Wisconsin. The calculated total number of bacteria in the bottom deposits was much greater than the number in the water in the case of eutrophic and dystrophic lakes, and lower in the case of oligotrophic lakes. When the plate counts were plotted against sediment depth, there was a general tendency for the curves to drop markedly at first, more slowly beyond. According to Kuznetsov (1958) there is a definite dependence between trophic status of a lake and the number of bacteria in sediments. He found higher bacteria counts in eutrophic lakes than oligotrophic lakes. Bordovskiy (1965) noted that the granulometric composition greatly affects the distribution of bacteria in sediments and their physiological activity. A considerable portion of the bacteria in fine-grained sediments are in an absorbed state, whereas in coarser-grained sediments most bacteria are present in a free state between particles and in solution. Supposedly, the physiological functions of adsorbed bacteria are to some extent restricted in affecting changes in the sediment environment compared to the free state bacteria (Bordovskiy, 1965).

In summary, changes and alterations in sediments may occur after deposition to the extent which depends on the chemical environment, bottom current, source of materials, sedimentation rate and biological processes.

H. Sediment Properties Affecting Retention and Release of Phosphorus

Any change in the composition or state of lake sediments could affect the retention and release of P to the water phase. Livingstone and Boykin (1962) indicated that the high sedimentary P bound largely by sorption reactions appeared to be the mechanism that limited the rate of biological growth during the early phase of Linsley Pond history. The distribution of P in Linsley Pond showed a marked resemblance to that found in the English Lakes discussed by Mackereth (1966). Relatively high concentrations of P occurred in the early postglacial deposits, followed by a fall in concentration to the surface in a more or less irregular manner. Mackereth stated that the marked change in the sedimentary P concentration at the clay/postglacial interface suggested that solution followed by precipitation of P was an important mechanism in postglacial time concurrent with the formation of a stable soil system in the drainage basin. At the time of glacial clay deposition, the migration and precipitation of P was accomplished by direct removal and deposition of fine rock particles.

Mackereth felt the two major processes involved in the sedimentation of P were coprecipitation of P with oxidized Fe and Mn compounds and precipitation of P incorporated in the organic material synthesized in the lake. In Ennerdale sediment the profiles of Fe and P concentrations were inversely related as the sediment surface was approached; Fe rose steadily in concentration, while P decreased. Mackereth explained that the precipitation efficiency for P in the Ennerdale basin has not been influenced by variations in the Fe-Mn cycle, but the precipitation of P was largely biological and relatively constant. On the other hand, Mackereth believed that the P concentration was directly related to Fe and Mn distribution in the Windermere and Esthwaite sediment and that the P minimum in the core profile resulted directly from the loss of Fe from the lake basin at that time.

Factors Controlling Phosphorus Sorption and Desorption. MacPherson et al. (1958) equilibrated P at different pH levels with sediments from several lake types. Maximal uptake of P (minimal P left in the water) occurred at pH 5.5 - 6.5. They found acid bog sediment released the largest quantity of P, while productive, medium productive and unproductive lake muds followed in that order. The adsorption of P on the lake sediments parallels that of a variety of solids (Carritt and Goodgal, 1954). A comparison with phosphoric acid dissociation curves indicates that maximum uptake of P by solids occurs in the pH range in which $H_2PO_4^-$ ion is predominant. Murrman and Peech (1969) observed, for any given soil, the amount of labile P in the soil and the concentration of P in the soil solution both reached a minimum value at about pH 5.5 and increased rapidly as the pH increased or decreased from this value. The adsorption of P on sediments and soils is often represented by an empirical adsorption isotherm. But as Carritt and Goodgal (1954) noted, the adsorption isotherm expression gives a concise analytical expression for the experimental facts, rather than a clear-cut picture of the mechanism of adsorption.

The sorptive properties of soil minerals have been studied in considerable detail by agronomists; they have been especially interested in P fixation. Hsu (1965) noted that recent studies on P fixation describe the mechanism as either precipitation or adsorption. According to Hsu, whether the process is precipitation or adsorption is dependent on the size of the polymer, which in turn is dependent on pH and the solution P concentration. In common soils, because of the effect of pH, surface-reactive amorphous Al and Fe hydroxy-polymers dominate the process of P fixation rather than discrete precipitation of Al^{+3} or Fe^{+3} compounds in solution. For example, in slightly acidic or neutral medium (pH 6-7) of dilute P solution (such as in sediments), amorphorus Al (or Fe) compounds are stable and P is adsorbed on the surface. On the other hand, in an acidic medium (pH 4) precipitation of Al might occur with a high concentration of P (Hsu, 1965).

Based on the pH-solubility relationship of soil phosphates when compared with those of known P minerals, it is generally accepted that the inorganic P is dominantly bonded to Al and Fe in acid soils, and mainly bonded to Ca in calcareous soils (Chang and Jackson, 1957; Hsu and Jackson, 1960). Lindsay and Moreno (1960) developed a solubility diagram for several pure Fe, Al and Ca compounds. Although the resulting solubility diagram indicated the importance of pH on all the systems, Lindsay and Moreno suggested that kinetic considerations during equilibration in soils could more often than not preclude the obtaining of solubility data which would correspond to any known solubility product. Hsu and Jackson (1960) gave evidence that the transformations of P in soils were mainly controlled by pH. Where strongly acidic, highly weathered soils underwent an increase in pH by $CaCO_3$ addition, a slow back-transformation to Ca-P occurred while considerable Al-P and Fe-P persisted. They found that reducing conditions in soils promoted the formation of Al-P instead of Fe-P. The Ca, Al and Fe phosphates in soils and sediments are mixtures of compounds of some complexity. Hsu and Jackson (1960) plotted the solubilities of these three compounds as a function of pH. On the basis of solubility products, Al-P and Fe-P solubility approximately equaled Ca-P between pH 6 and 7. The solubilities also depended on the activities of such other compounds as gibbsite, Al silicates, Fe oxides and $CaCO_3$ present. Above pH 6-7, Ca-P was more stable than either Fe-P or Al-P especially in the presence of $CaCO_3$. Frink (1969) found that a number of chemical changes occurred as sediment was transported from the acid watershed to the neutral lake environment. The Al-P and Fe-P were the major storage forms in the acid watershed soils, while there was a shift towards Ca-P form in the neutral sediments. One effect of liming on the form of P in soils is to favor the formation of Ca-P and to release P through the repression of Fe and Al compounds (Chang and Jackson, 1958). Work on the sorption of phosphate by $CaCO_3$ was reported by Cole et al. (1953). Their work demonstrated a surface sorption of P on $CaCO_3$ particles at low concentrations of P in solution, and a precipitation reaction at higher concentrations. Zicker et al. (1956) added $CaCO_3$ to the water phase of mud-water systems to reduce the amount of soluble P in solution. However, Bailey (1968) noted that $CaCO_3$ or the clay minerals, kaolinite and montmorillonite possess less capacity to fix P than $Fe(OH)_3$ and $Al(OH)_3$.

The possible formation of hydroxyapatite in the pH range of natural waters by the conversion of $CaCO_3$ to apatite was considered by Stumm (1963). He calculated the equilibrium constant for such a reaction by combining several reactions and then computed a free energy for the conversion of $CaCO_3$ into apatite. Stumm suggested that a negative ΔF obtained from this reaction could be of significance in connection with eutrophication of lakes, because it would suggest that the P distribution in a lake can be interpreted as a heterogeneous distribution equilibrium between sediments and the lake, i.e., any addition of P would lead to a progressive accumulation of P in sediments. However, the fact that apatite can be present as inclusions in soil minerals instead of discrete grains may exert a considerable influence on the availability of P and on the rate and pattern of inorganic P transformations in soils and sediments (Syers et al., 1967). Frink (1969) observed that Ca-P was associated with the coarser fraction of sediment in a small eutrophic lake in Connecticut and the Ca-P fraction decreased with increased water depth.

The capacity of lake sediments for sorption of P was demonstrated by Harter (1968). He used various concentrations of P in water and mixed them for a short time with 0.1 gram of sediment. Based on the amounts of P extracted with NaOH and NH_4F from the treated mud, Harter found the addition of less than 0.1 mg P/g of sediment resulted in a tightly bonded form of P occurring probably as Al-P. When more than 0.1 mg P/g was added, the additional P was in a more loosely bond form of P extractable in NH_4F. Harter concluded that the capability of the sediment to adsorb considerable loosely bound P means large influxes of P into the lake may be held temporarily and subsequently released to growing plants and algae. Hsu (1965) found when the surface of amorphous Fe and Al compounds were nearly saturated with P, the adsorbed P may be highly available to plants. On the other hand, the adsorbed P may be less available when a small amount of P is retained by a large amount of amorphous Fe and Al compounds. Carritt and Goodgal (1954) examined the P-solids system in Chesapeake Bay sediments and suggested that low salinity and pH and high turbidity of the fresh river water favored the formation of the P sorptive complex. In estuaries mixing of these waters with sea water presents an environment of higher salinity, pH and concentration of competing ions, factors which favor the regeneration of P. Carritt and Goodgal also suggested that during desorption of P, both the amount of P and the rate of removal from the complex will depend upon the length of time the complex has had to form. With a long contact time a greater fraction of the P will have diffused into the solid and so will be slower [illegible] return to solution when environmental conditions change in a direction favoring desorption. Kafkafi et al. (1967) studied the desorption of P on kaolinite. If the P was adsorbed in very small increments, some of it was converted directly into a fixed form. In the presence of large concentrations of P, all the adsorbed P became exchangeable. Experiments were made on the effects of pH, P concentration, particle size, Fe and organic matter on the adsorption of phosphate by estuarine bottom deposits by Jitts (1959). The ability of the sediment fractions to adsorb P showed an inverse relationship with particle size. While the presence of organic matter depressed P uptake, the increase in concentration of Fe increased the sorption of P. Olsen and Watanabe (1957) found that P sorption was closely related to surface area. Acid soils retained more P per unit surface than alkaline soils, and acid soils also held P with greater bonding strength than alkaline soils. Isotopically exchangeable P as determined by isotopic dilution is a useful index of active P in sediments. The extent to which the P fraction undergoes isotopic dilution is taken as an estimate of the fraction's surface activity. According to Tandon and Kurtz (1968), the specific activities of the P fractions in widely different soils followed the sequence of Al-P > Fe-P > Ca-P. For instance, Ca-P has more slowly exchangeable components than Al-P.

Oxidation-Reduction Effects. Rittenberg et al. (1955) observed from the distribution of phosphate in the interstitial waters of cores from the Santa Barbara and Catalina Basin that Eh played a major role in the solubility equilibria. In the former sediment, which was strongly reducing throughout, phosphate concentration increased rapidly from the surface downward; in the latter, phosphate increased markedly only in the zone of negative Eh which started about 80 cm below the surface of the core. They found in the sediments investigated that deposition of P took place in an environment of relatively low pH, low organic content and an Eh near zero. Soluble P accumulated in an environment of low Eh and relatively high pH and organic content. The presence of organic compounds which form chelation complexes with Fe and Al ions are reported to have the effect of decreasing the extent of phosphate precipitation by these ions (Struthers and Sieling, 1950, and references cited therein). Savant and Ellis (1964) noted, in submerged soil, the solubility of soil P increased with the development of reducing conditions when Fe-P was the main constituent of soil P. A negative linear relationship between available P and redox potential was distinct in slightly acid silt loam soil, but the relationship was not as evident in the calcareous silt loam. Their experiments showed that organic matter in submerged soil accelerated the rate of decrease of redox potential. Mortimer (1941; 1942) proposed that the adsorbent properties of the oxidized mud surface were largely due to the presence of colloidal ferric complexes and that removal of complexes on reduction of the mud surface liberated adsorbed ions, including phosphate, to the overlying waters. Al, unlike Fe, does not respond to changes in redox potential and thus the stability of Al-P in the sediments would be higher than similar Fe-P during periods of reduction in stratified lakes.

Effect of Organics. Swenson et al. (1949) observed that several organic anions were effective in preventing P from combining chemically with Al and Fe or by replacing the chemically combined P. Humus and lignin were effective in replacing P from the basic Fe-P, probably because of the formation of stable compounds or complexes between active Fe and humus or lignin. Struthers and Seiling (1950) found each organic acid investigated differed from the other in its effectiveness in preventing P fixation by Fe and Al at different pH values. The organic acids used by Struthers and Seiling occur in soils as a result of the action of microorganisms on organic matter. The most effective substances were those that formed metal-organic complex molecules of great stability: citrate, tartrate oxalate, malate, and lactate. The dominance of active Fe or Al in the system will depend largely on pH, redox potential and stability of the ligands formed. In calcareous sediments the decrease in P fixation with organic and carboxylic acids from the organic matter would not be as important so long as solid-phase $CaCO_3$ remained in control of pH.

Only a minor part of the organic P of soils appears to be present as nucleic acids and phospholipids. Inositol phosphate form a major part of the soil organic P thus far identified (Bailey, 1968). Jackman and Black (1951) found that Fe and Al salts of inositol phosphates were very insoluble in an acidic medium. Because the pH solubility curves were very similar to the inorganic orthophosphates, organic compounds such as phytin and their derivatives should be fixed in soils as insoluble Al, Fe and Ca salts.

Phosphorus Sorption and Release at Sediment-Water Interface. The sorption and release of sedimentary P will depend to some extent upon the depth to which P effectively exchanges with the water. The loss of added P fertilizer to a small unstratified Scottish loch was studied by Holden (1961). Mud core samples showed that P penetrated downwards through the mud about 2 cm after 8 months and 3 cm in 48 months. Most of the P removed (85 percent) remained in the upper aerobic zone of the mud (2 cm below sediment-water interface) and was converted to organic forms, presumably by bacteria. Zicker et al. (1956) found when radioactive superphosphate fertilizer was placed at various depths below the mud surface, the percentage as well as the amount of P released to the water was small with no P released from depths greater than 1/4 inch below the mud surface. Agitation by stirring the muds resulted in approximately twice the concentrations of P in the water phase compared to undisturbed systems. The depth of an oxidized microzone of ferric gels across the mud-water interface was believed by Mortimer (1942) to be maintained by molecular diffusion of oxygen into the mud, to a distance depending almost wholly upon reducing power of the sediment in a given lake. Mortimer proposed that the thickness of the oxidized layer of mud during water circulation e.g., after autumn overturn, could be related to the productivity of a lake. Hayes et al. (1958) questioned whether the oxidized layer is as thick as measurements suggest. Hayes presented evidence that the real oxidized layer of sediments from eastern Canadian lakes is one mm or less thick. Hutchinson (1957) felt the seasonal presence or disappearance of an oxidized microzone in the sediments could be an important influence on the chemical classification of lakes. Gorham (1958) presented evidence that the thickness of the oxidized microzone at the surface of lake mud may depend upon turbulent displacement of the uppermost sediments into the overlying aerated water. The sediments containing Fe become oxidized and then settled to the surface muds forming the oxidized microzone.

Biological Factors. Bottom dwelling organisms and the abundant bacterial flora exert an effect on the transformation of organic matter and on the alteration of physicochemical properties in sediments which in turn may influence sorption-desorption reactions of P. Aerobic bacteria are dominant in the upper layers, but below the upper layers the role of anerobic bacteria increases. The redox potential of sediments is particularly affected in the zone of maximum bacterial activity (Zobell, 1946). Hayes and Phillips (1958), using both cores and shaken bottom sediments, presented evidence that, in lakes, bacteria may compete with the sediments for P, reducing the rate of exchange of P between water and sediments, and retaining P in water as bacterial protoplasm. Pomeroy et al. (1965) felt the exchange of sedimentary P that was incorporated in bacterial protoplasm was small because the organisms involved were beneath the surface of the sediments; however, the authors thought the biological P would be exchanged with the water if the sediments were suspended. The distribution of ^{32}P between mud and water was studied by Hayes and Phillips (1958) who found the exchange of P with the mud of natural and artifically prepared Jenkins cores was the same. Thus, the destruction of natural physicochemical and biological layering of the surface muds did not influence the exchange pattern.

I. Other Wisconsin Lake Sediment Studies

Surface Muds. Juday, Birge and Meloche (1941) analyzed the surface muds of 18 lakes in northern Wisconsin and 3 lakes in southern Wisconsin for Si, Fe, Al, Ca, Mg, P, S, carbonate and organic carbon. The same components were measured by Black (1929) for several lakes in northern Wisconsin. Steiner and Meloche (1935) determined the lignin content of Wisconsin lake sediments and found the organic matter contained 30 to 48 percent lignin; higher percentages of lignin were found in northern than southern Wisconsin lakes. Studies on the composition of the bottom muds in Lake Mendota were made by Levihn (1951) and Kaneshige (1952). Samples of the bottom muds were collected and analyzed for soluble and total P, free ammonia, nitrate, organic N and total Fe. Results of these studies were presented by Rohlich (1963). The oxidation-reduction potentials and pH of lake waters and sediments were measured by Allgeier et al. (1941) for several lakes in northern Wisconsin; the pH of surface muds measured in situ ranged from 5.6 to 6.8.

Cores. Twenhofel cored lakes in Wisconsin which included Mendota (Twenhofel, 1933), Monona (Twenhofel, 1937), Devils (Twenhofel and McKelvey, 1939), Crystal (Twenhofel and Broughton, 1939), Little Long (Twenhofel and McKelvey, 1942), Grassy (Twenhofel et al., 1942) and Trout (Twenhofel et al., 1945) lakes. Most often, Twenhofel and his co-workers analyzed only the top, middle and bottom of each core; they noted the physical characteristics and minerology and determined chemical components such as inorganic and organic carbon, Si, Al, Fe, Mn, Mg and Ca in the sediment cores. Twenhofel et al. (1944) collected complete core sequences of the postglacial sediments for several lakes; the maximum thickness of the sediments was 9.2 m for Grassy Lake, 4.7 m for Nebish, 5.9 m for Little John and 13 m for Allequash lake. In addition, Twenhofel et al. (1945) and Twenhofel and Broughton (1939) observed the thickness of sediments were 4.8 m for Trout Lake and 3 m for Crystal Lake, respectively. Sawyer et al. (1944) obtained cores from Lake Mendota as well as the three lower lakes. To evaluate the quantity of N and P that could be released from the sediments, Sawyer et al. leached one liter samples of surface mud cores from the lower Madison lakes with Lake Mendota water. From the slope of the curves for nutrient release after 50 or 60 days digestion, it appeared the release of nutrient materials from bottom muds was very slow. Conger (1939) studied the diatoms in the cores from Crystal Lake and found unexpected diversity both in biological stratification and in the horizontal distribution of diatoms. The diatom flora was more diverse at the bottom of the cores, and several middle samples were dominated by Fragilaria construens, indicating rich "blooms" of this species. Acid tolerant diatoms indicated a change toward greater acidity in the upper sediments.

Studies on pollen chronology, bacteria and benthos of Wisconsin lakes and bog sediments are discussed in a review paper by Frey (1963).

J. Summary

Although several chemical studies have been performed on postglacial sediments and interpreted on the basis of long-term trends (Brown, 1969; Gorham, 1961; Horie, 1966; Hutchinson and Wollack, 1940; Kendall, 1969; Livingstone and Boykin, 1962; Pennak, 1963; Vallentyne, 1969), few investigators have given sustained study to the most recent changes in lake history. Additional studies are needed to examine the effect man has played in causing changes in the sedimentary environment. Episodes involving the dynamic aspects of lakes will continue into the future, but the rates, dates and relative changes that have occurred will remain speculative until more data are collected about the past history of lakes. Studies need to be conducted on the P sorptive-desorptive capacity and nutrient leaching potential of the pre- and postcultural sediments in order to suggest limnological implications due to culturally-influenced changes in chemical composition of the sedimentary profiles. Closer attention needs to be given to such complexities as sedimentation rates mixing of sediments and replicate coring within the same lake in order to better evaluate and interpret concentration vs. sedimentary depth profiles.

CHAPTER III

EXPERIMENTAL PROCEDURES

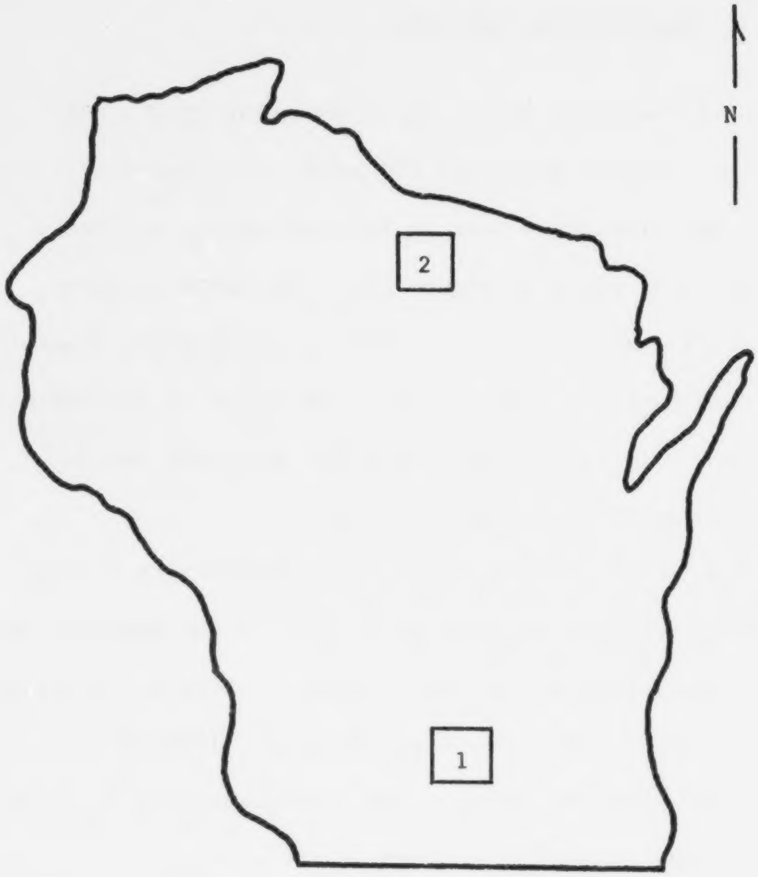
A number of lakes in northern and southern Wisconsin were studied in varying detail. This chapter describes the lakes, sampling locations, laboratory techniques and procedures used in this endeavor. A general view of the lakes studied is given in Figure 3.1. The lakes in Vilas and Oneida counties are situated in stony, sandy, noncalcareous, glacial drift. The upper ground water is notably soft. The soils of the Madison lakes drainage basin are a silty loam which overlie sandstone and dolomite. Devils Lake is situated in a quartzite region.

Some hydrologic, morphometric and chemical characteristics of each of the study lakes are summarized in Table 3.1. Most of the hydrographic and morphometric data was obtained from the Wisconsin Conservation Department surface water resources reports (Poff and Threinen, 1962; Black et al. 1963; Andrews and Threinen, 1966). The water chemistry data was obtained by Water Chemistry students and staff in 1965-1967.

A. Natural Environment

The coring stations on subsequent lake maps are indicated by black circles.

Lake Mendota is a hard-water eutrophic lake formed by morainic damming of the preglacial Yahara River valley (Twenhofel, 1933). In addition to several springs, three principal streams enter the lake. The lake currently receives domestic drainage from agricultural lands, urban runoff, and some municipal and industrial waste effluents contained in entering streams. Four cores were taken from Lake Mendota in



Area	County	Lakes
1	Dane, Sauk	Mendota, Monona Wingra, Devils
2	Vilas, Oneida	Trout, Little St. Germain Weber, Sparkling, Minocqua Little John

Figure 3.1 State of Wisconsin Showing General Location of Lakes Studied.

Table 3.1 Some Limnologic, Hydrologic and Morphometric Characteristics of Study Lakes.

Characteristic	Mendota	Monona	Wingra	Devils	Trout	Minocqua	Little St. Germain	Weber	Little John	Sparkling
Productivity classification [a]	eutrophic	eutrophic	eutrophic	oligotrophic-mesotrophic	oligotrophic-mesotrophic	eutrophic	eutrophic	oligotrophic	mesotrophic-eutrophic	oligotrophic-mesotrophic
O_2 in hypolimnetic water [b]	O_2 depletion summer and winter	O_2 depletion summer and winter	O_2 present summer and winter	O_2 depletion in summer	some O_2 depletion summer and winter	O_2 depletion summer and winter	O_2 depletion summer and winter	O_2 present summer and winter	some O_2 depletion in winter	some O_2 depletion in summer
Alk. (mg $CaCO_3$/l	150-180	157-189	135-184	20-25	40-46	44-60	35-65	3-6	33-52	30-36
Cond. (µmhos/cm/20° C)	300-400	---	430-515	72-80	70-87	80-150	70-90	6-20	73-100	55-65
Water source [c]	D	D	D	S	D	D	D	S	Spr	S
Watershed area (acres)	169,500	196,000	5370	3520	25,600	51,200	9350	128	704	640
Surface area (acres)	9730	3335	345	384	3911	1285	959	11	166	127
Maximum depth (m)	25	21	4.25	13.5	35	18.3	17	13.5	6.0	19.5
Mean depth (m)	12.2	8.5	1.6	---	13.7	---	3.88	7.24	3.77	11.3
Shoreline development [d] factor (D_L)	1.58	1.54	1.42	---	1.83	3.68	3.23	1.14	1.65	1.31

[a] Based on an observed aquatic weed and algal growth, O_2 depletion in hypolimnion, alkalinity and conductance of lake water.

[b] Water chemistry data represents a range of values obtained from deep area of lakes during summer, fall and winter sampling trips in 1965-1967; values will depend on season of year, depth of water, snow cover and location within lake.

[c] D = drainage lake has outlet and inlet. S = seepage lake has no outlets and inlets; intermittent outlet may be present; water level maintained by groundwater and basin seal. Spr = spring lake seldom has inlet, but always has outlet of substantial flow.

[d] D_L is the ratio of the length of shoreline to the circumference of a circle equal to the area of the lake; the quantity can be regarded as a measure of the potential effect of littoral processes on the lake. With increased littoral area greater biological productivity can be expected.

progressively deeper water following a transect from University Bay to the center of the lake as shown in Figure 3.2. University Bay has two inlets: an inlet coming from a pumping station of lowland drainage and a small creek, University Creek, which serves as a storm sewer for urban Madison.

Lake Monona is the second in the series of morainic dammed lakes of the Yahara River. During the periods of 1898-1936 and 1942-1950, Lake Monona received the treated sewage from the City of Madison. Copper sulfate was systematically applied from 1925 through 1953 to control algae blooms (Nichols et al. 1946). The pollutional history of the Madison lakes is discussed by Stewart and Rohlich (1967), Sarles (1961) and Sawyer et al. (1944). The bathymetry and coring stations of Lake Monona are given in Figure 3.3.

Lake Wingra is a small, shallow, eutrophic lake. The present water supply of Lake Wingra is provided by surface drainage, springs and storm sewers. Many springs which provided Lake Wingra with a steady flow of water have been replaced as sources of water by storm sewers (Noland, 1951). Nearly 200 acres of shrub and marsh land adjoin the lake. Some limnological aspects of Lake Wingra are reported by Tressler and Domogalla (1931). A single core was obtained in the deep basin in the east-central part of the lake in 3.4 m of water.

Devils Lake is an oligotrophic-mesotrophic lake of soft clear water. The lake has only two small streams entering it and no streams leaving it. Evaporation and seepage control the losses (Black, 1968). A single core was taken from the southern basin in 13.1 m of water.

Trout Lake is a deep, clear, oligotrophic-mesotrophic lake situated in state forest land. Four small streams flow into Trout Lake and one stream flows out. There is considerable flow into the lake by seepage

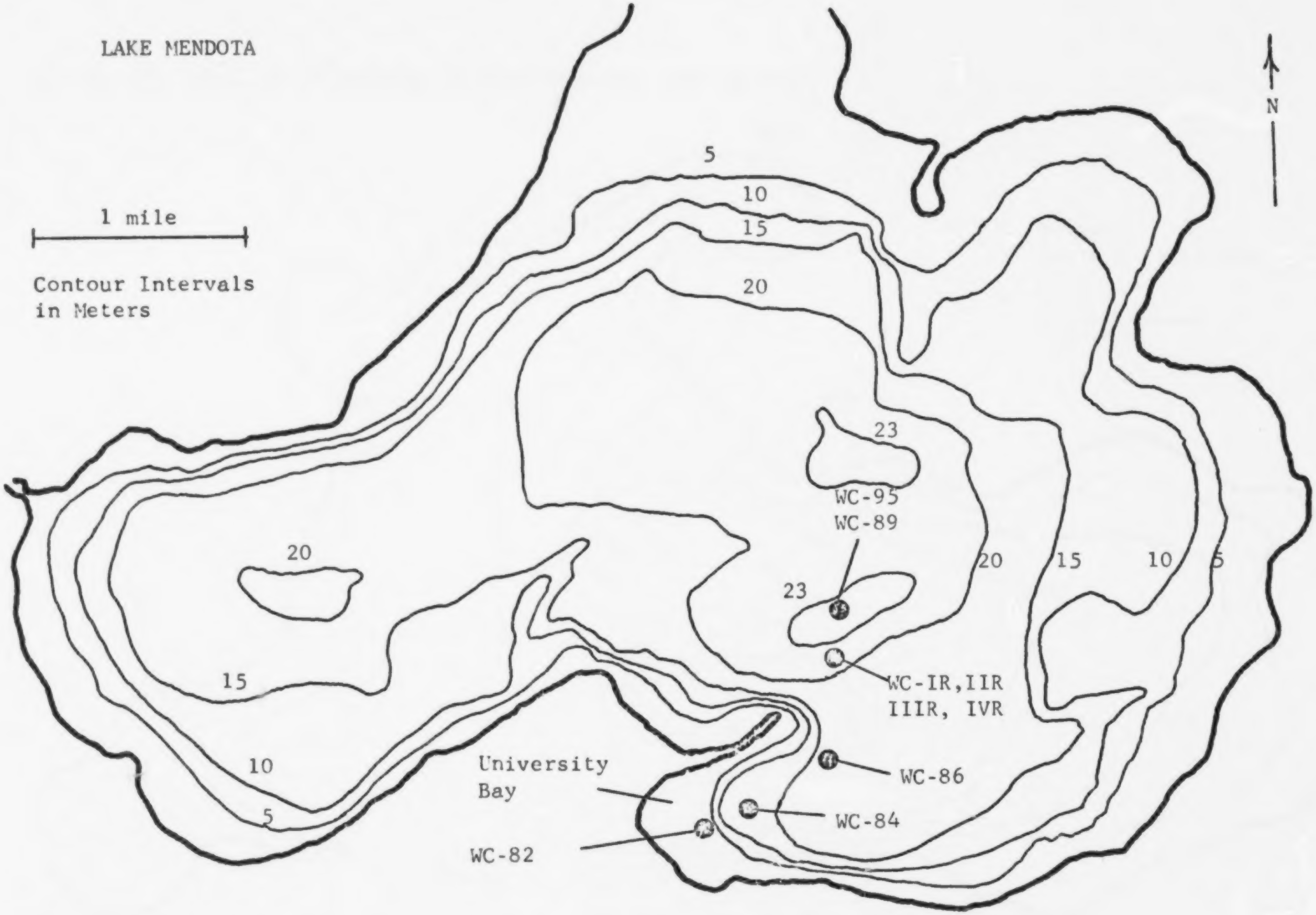

LAKE MENDOTA
1 mile
Contour Intervals
in Meters
N
5
10
15
20
23
23
20
WC-95
WC-89
WC-IR,IIR
IIIR, IVR
WC-86
WC-84
WC-82
University
Bay
20
15
10
5
15
10
5

Figure 3.2 Bathmetry and Coring Locations for Lake Mendota.

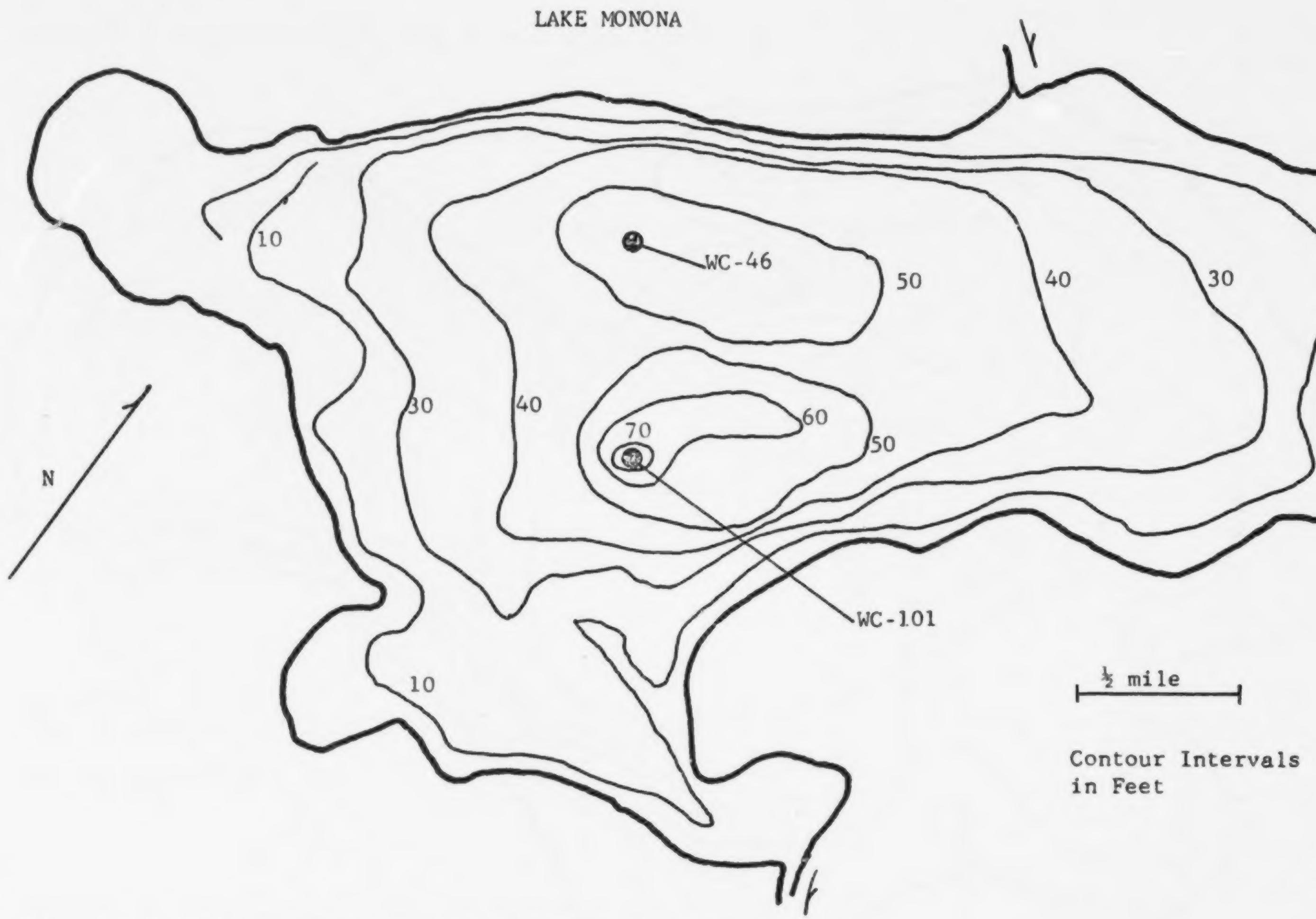

LAKE MONONA
10
WC-46
50
40
30
10
30
40
70
60
50
N
WC-101
10
½ mile
Contour Intervals
in Feet

Figure 3.3 Bathymetry and Coring Locations for Lake Monona.

(Twenhofel et al., 1945). Cores were taken from the central basin of both North and South Trout Lake. A bathymetric map and coring stations of Trout Lake are shown in Figure 3.4. The map includes an insert of the Trout Lake region showing the location of Sparkling, Weber and Little John lakes.

Minocqua is a soft-water drainage lake having slightly acid, light-brown water of moderate transparency. Aquatic vegetation and algae are problems in parts of the lake basin. Fifteen resorts, four marinas, 271 dwellings and the town of Minocqua are located on the shores. Less than 4 percent of shoreline is public. During the period 1935-1964 the sewage from a secondary treatment plant serving the town of Minocqua was discharged to a small bay located near the town which then flowed to the northwest bay of Lake Minocqua (F.H. Schraufnagel, Personal Communication, Wis. Dept. of Natural Resources, 1969). Water levels are maintained by a water control structure with a 4-foot head on the outlet of Keweguesaga Lake. A bathymetric map and coring stations are shown in Figure 3.5.

Little St. Germain is a shallow eutrophic lake with an extensively developed shoreline. On the 13 miles of shoreline there are 100 private cottages and 46 resorts. Aquatic weed growth has been a problem on the lake. The inlet and outlet streams are considered navigable water. A 5-foot dam maintains water levels, and the upper 22 inches is used for water storage and low flow augmentation of the Wisconsin River. A bathymetric map and coring stations are shown in Figure 3.6.

Weber Lake is a small, oligotrophic, seepage lake, having slightly acid water. There are no private or commercial developments on the shoreline. The lake has been free of modifying activity of campers and fishermen, but scientific studies involving the addition of fertilizer

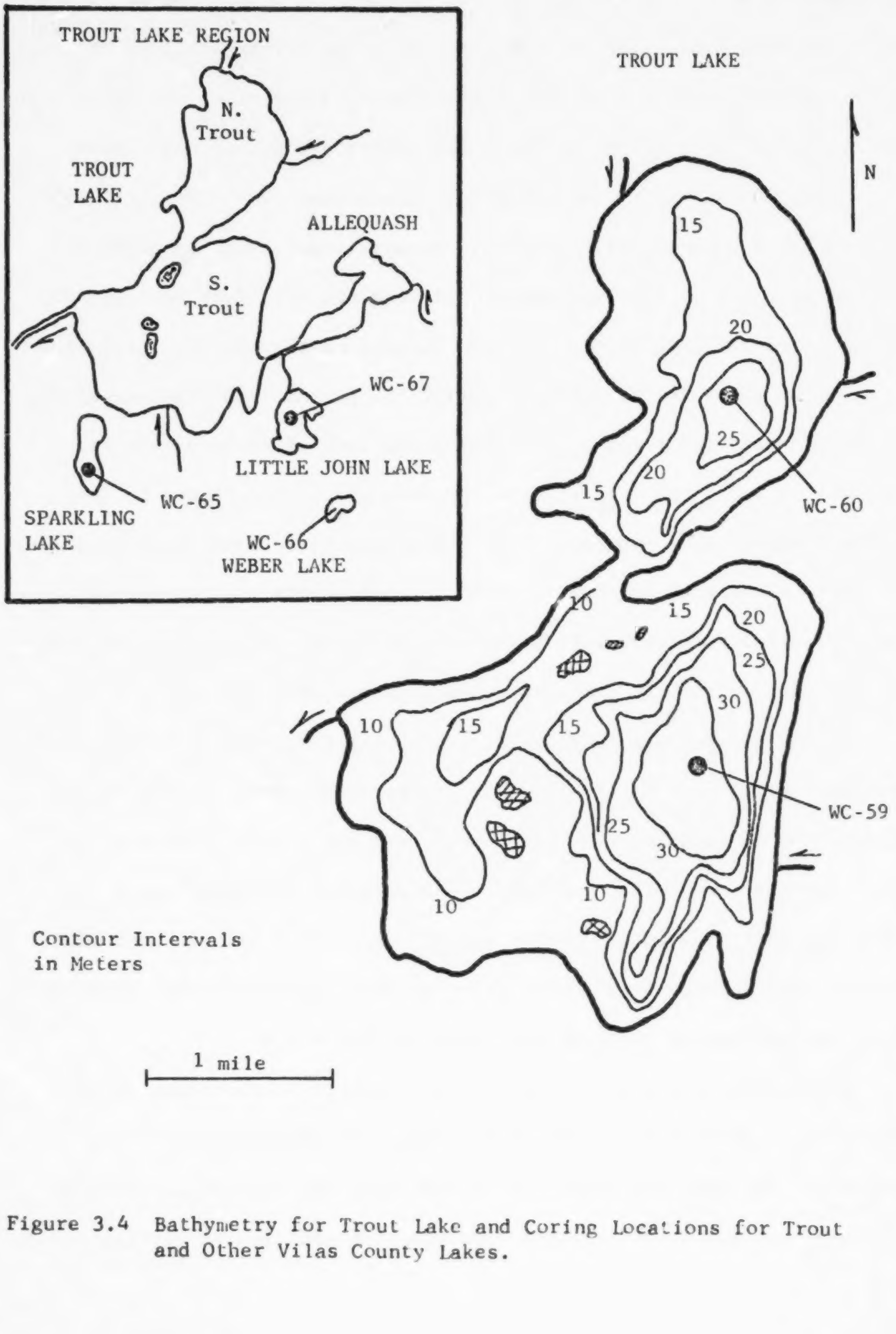

TROUT LAKE REGION
N. Trout
TROUT LAKE
ALLEQUASH
S. Trout
WC-67
LITTLE JOHN LAKE
WC-65
SPARKLING LAKE
WC-66
WEBER LAKE
TROUT LAKE
N
15
20
25
20
15
WC-60
10
15
20
25
30
10
15
15
WC-59
25
30
10
10
Contour Intervals in Meters
1 mile

Figure 3.4 Bathymetry for Trout Lake and Coring Locations for Trout and Other Vilas County Lakes.

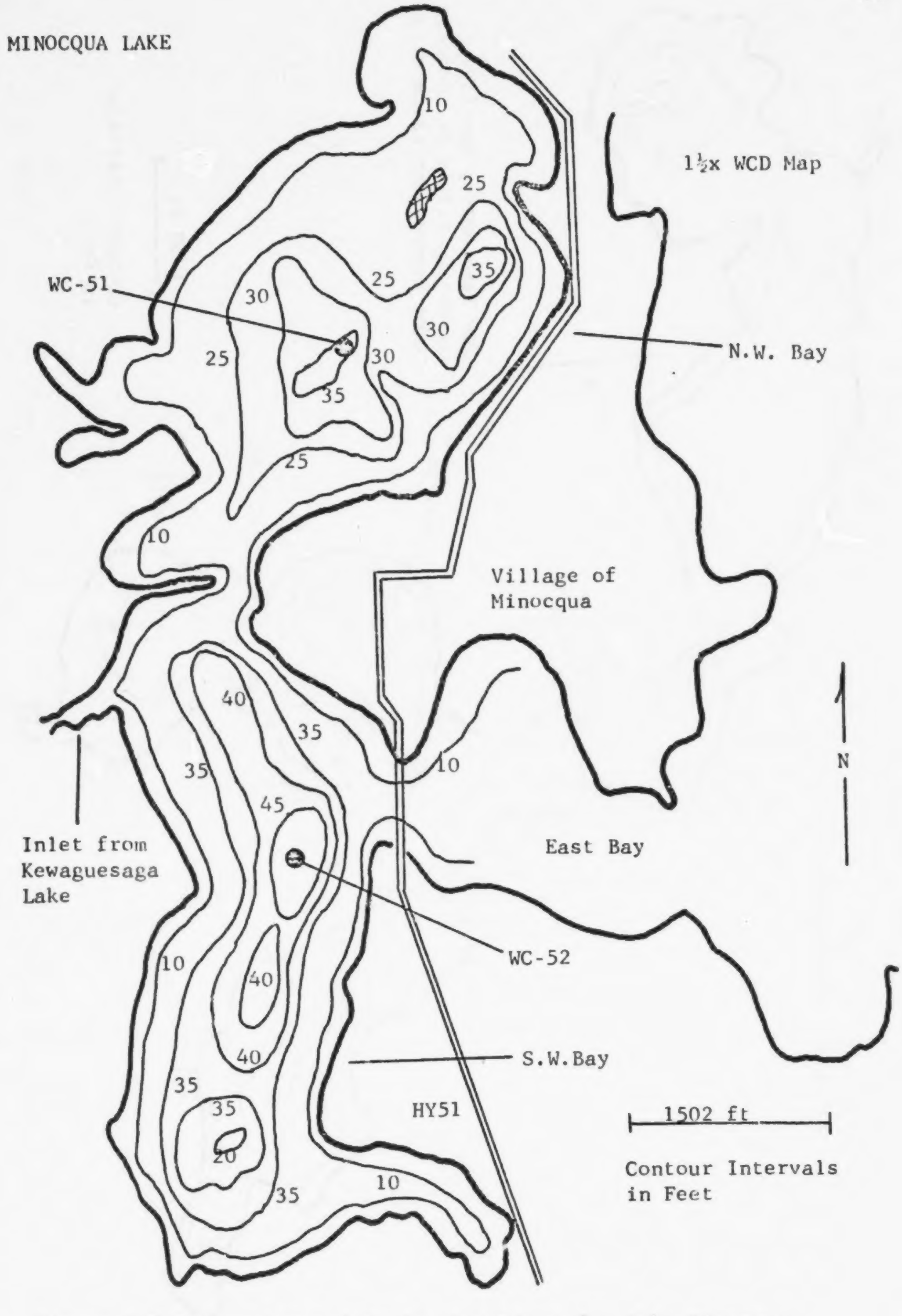

MINOCQUA LAKE
1½x WCD Map
10
25
35
25
30
30
WC-51
25
30
35
25
N.W. Bay
10
Village of Minocqua
40
35
35
10
N
45
East Bay
Inlet from Kewaguesaga Lake
WC-52
10
40
40
S.W.Bay
35
35
HY51
1502 ft
20
35
10
Contour Intervals in Feet

Figure 3.5 Bathymetry and Coring Locations for Lake Minocqua.

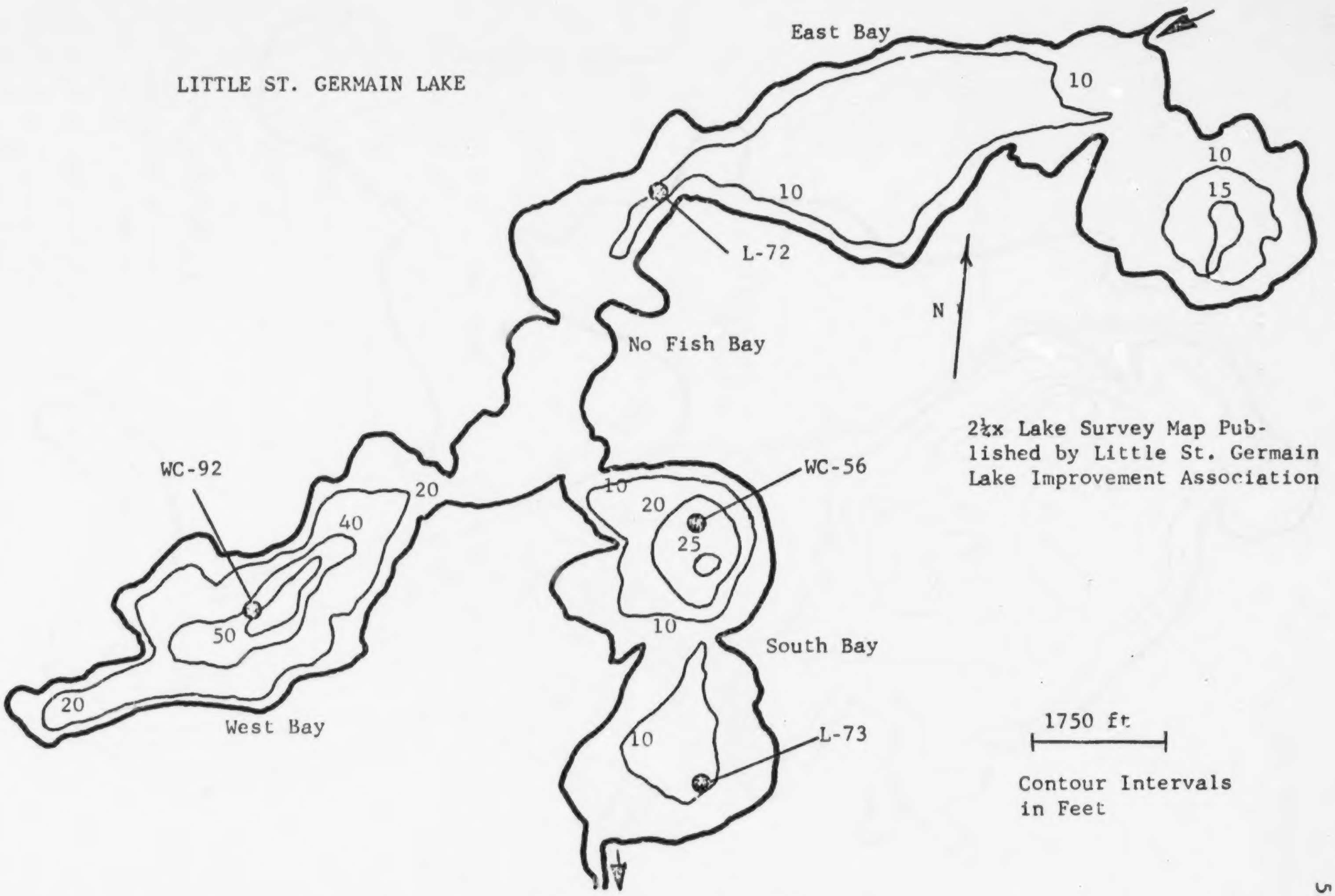

LITTLE ST. GERMAIN LAKE
East Bay
10
10
15
10
L-72
N
No Fish Bay
2¼x Lake Survey Map Published by Little St. Germain Lake Improvement Association
WC-92
20
40
50
20
West Bay
WC-56
10
20
25
10
South Bay
10
L-73
1750 ft
Contour Intervals in Feet

Figure 3.6 Bathymetry and Coring Locations for Little St. Germain Lake.

were carried out from 1932-1939. A core was obtained from the center of the lake in 12.6 m of water.

Little John Lake is a shallow spring-fed lake of high fertility. There is a small outlet stream. Most of the shoreline is public frontage. A core was obtained from the 5 m basin in the center of the lake.

Sparkling Lake is a oligotrophic-mesotrophic seepage lake surrounded by forest. The shoreline is 87 percent in public ownership. A core was obtained in the south-central basin in 18.8 m of water.

B. Field Sampling Methods

Sediment Collection. Surface sediments were collected from the lakes by use of an Ekman dredge. Sediment core samples of one meter length were collected by a piston-operated coring device of large diameter (3.5 inch i.d.). The design and operation of the piston corer was described in detail by Wentz (1967) and Bortleson (1968). A sampling platform was provided by a converted Army Amphibious Dukw. A 10 m core from Lake Mendota was taken using four connected 10-foot lengths of galvanized 1-1/2 inch (i.d.) pipe. The corer was piston-operated with 1-1/2 inch (o.d.) plastic cellulose acetate liners inserted in the pipe. The cores were extruded immediately in 5-cm lengths and placed in commercial polyethylene "sandwich" bags. The samples were frozen until commencement of the analysis.

Two long cores were collected from Little St. Germain by the University of Wisconsin Geology Department and the Wisconsin Geological and Natural History Survey by using a modified Livingston peat sampler of 2-inch diameter up to one meter in length. Overlapping lengths of core were taken to yield complete sequences of sediment. The cores were extruded, cut into five-inch segments, put into glass jars and later refrigerated.

C. Analytical Procedures and Apparatus

Preanalysis of Sediments.

The steps that were followed to prepare the sediments for dry or wet analysis are outlined below.

Drying and Grinding. After thawing, the samples were stirred in a Waring blender to make each sample homogeneous. Samples needed for chemical analysis and percent solids determination were placed in petri dishes and dried at 105°C for 12-16 hours in a Fisher Isotemp Oven. A simultaneous density measurement of the sediment was obtained by taking the sample with a 50 cc, large orifice, plastic syringe. The sample was ground with a porcelain mortar and pestle and passed through a 100-mesh screen. After grinding, the samples were reintroduced into the oven for 3-4 hours at 105°C. For wet analysis, such as determining exchangeable ammonium, samples were obtained and run immediately.

Digesting. The sediment was brought into solution using HF predigestion followed by $HClO_4$-HNO_3 digestion. Sediment samples (0.500 g) were placed in 35 ml polypropylene beakers and heated on a steam bath in the presence of 5 ml of 48% HF. Polypropylene beakers were supported over the steam bath by a lucite plate with holes for the beakers. After heating the solution for 10-12 hours, the residue was transferred to a 100 ml Kjeldahl flask and digested with 10 ml of $HClO_4$-HNO_3 (3 parts 60% $HClO_4$ and 5 parts concentrated HNO_3 by volume) using an AMINCO (American Instrument Company) 12-burner digester assembly set up in the fume hood. Heating of the digestion mixture was continued until heavy white fumes of

$HClO_4$ appeared. A trap was provided to catch the $HClO_4$ fumes.

Filtering and Diluting. After the digestion, the samples were cooled, filtered through Whatman #2 filter paper into 100 ml volumetric flasks, diluted to volume and mixed. Aliquots were taken from the 100 ml dilution volume representing 0.500 g of sediment for total P, Fe, Mg, K, Ca, Mn and Al.

Chemical Methods.

All reagents used were ACS grade chemicals.

Total carbon was determined by a dry combustion technique using a LECO (Laboratory Equipment Corporation, 1959) low carbon analyzer (Model 589-400) and LECO induction furnace. The CO_2 released by combustion of carbon compounds and decomposition of carbonate is measured by a thermal conductivity cell. The sample in a carbon-free ceramic crucible containing iron and tin chip accelerator is combusted in 3 minutes at approximately 1500°C with an O_2 flow rate of 1.5 liter/min. The gases are reacted with a catalyst to oxidize CO to CO_2, and with MnO_2 to remove sulfur and nitrogen oxides. The recovery of carbon by dry combustion of pure compounds of glucose and $CaCO_3$ was 98-100 percent.

A direct weighing of the high carbon-containing sediment samples was not practical since the optimum working range for the low carbon analyzer is 0.030 to 0.50 mg of carbon. In order to obtain at least a 30 mg weighing, the sediment samples were diluted with powdered silica (140 mesh) 10:1 or 20:1. Several blank determinations containing powdered SiO_2 showed no detectable carbon. Homogeneity of the powdered silica and sediment sample was effected by shaking and vibrating the mixture together in a 1-oz bottle. A mixture of $CaCO_3$ and SiO_2 was checked for homogeneity using subsamples for carbon determination. The carbon recovery was 98-100 percent (Bortleson, 1968). A calibration line was established using either LECO standards or a $CaCO_3$-silica mixture containing 0.030, 0.15, 0.30, 0.45 and 0.54 mg carbon.

The output of the thermal conductivity cell was measured on an integrator clock or a Moseley Autograf (Model 680) recorder. A comparison of total carbon determinations using the integrator and peak height methods is shown in Table 3.2.

Table 3.2 Concentration of Carbon Observed in Sediment Using Peak Height and Clock Integrator Methods.

Sample	Replicates	Mean $\pm\sigma$ mg C/g Integrator Method	Mean $\pm\sigma$ mg C/g Peak Height Method
L. Mendota - WC 82 Section 5	5	149 ± 1.6 [a]	145 ± 2.6
L. Mendota - WC 82 Section 15	5	113 ± 3.3	114 ± 3.2
L. Mendota - WC 84 Section 4	5	103 ± 3.6	103 ± 3.5
L. Mendota - WC 84 Section 14	5	153 ± 3.2	150 ± 2.0

[a] Standard deviation,

Organic Nitrogen. Organic nitrogen was determined by semimicro Kjeldahl technique which involves three basic steps: 1) digestion of the sample to transform the nitrogen to $(NH_4)_2SO_4$, 2) distillation of ammonia gas freed from the ammonium sulfate by NaOH and 3) measurement of the distilled NH_3 by titration. The procedure is outlined by Bremner (1965) and described in detail by Bortleson (1968).

Exchangeable Ammonium. No generally accepted definition of exchangeable ammonium is available, but for analytical purposes in soils literature it is usually defined as ammonium which can be extracted by KCl (or K_2SO_4) solution at laboratory temperatures (Bremner, 1965). The extract from this treatment is analyzed by steam distillation methods. Alternatively, a sample can be treated with 2 N KCl and analyzed directly by the same methods. The possibility of interference by organic soil N compounds is clearly greater in this procedure than in those involving extraction, but analyses of a large number of soils have shown that the results by this direct procedure are in close agreement with those obtained using extraction procedures (Bremner, 1965). The procedure involves 1) steam distilling of a wet sample of sediment in the presence of 2 N KCl and MgO and 2) titrating the distilled NH_3. A wet sample of mud was placed in a 50 ml Erlenmeyer flask, stoppered and weighed. A separate sample was taken for percent solids determination in order to base the analysis on dry weight. After weighing, the sample was transferred to a 100 ml Kjeldahl flask to which was added 10 ml of 2 N KCl and 0.1-0.2 g of MgO. Small amounts of MgO were added to minimize the interference from alkali-labile organic N compounds. The sample was steam-distilled into an indicator boric acid solution and titrated with 0.01 N HCl.

Total Phosphorus. The P determination has two distinct phases: first, the preparation of a solution containing the sediment P or fraction thereof, and second, the quantitative determination of the P in solution. Two methods were used in the preliminary experiments to extract total P from the sediments: 1) $HClO_4$-HNO_3 digestion and 2) HF predigestion followed by $HNO_3H_2SO_4$ digestion. A comparative evaluation of these acid procedures for the determination of total P on Lake Mendota sediments is reported by Bortleson (1968). Syers et al. (1968) have compared several fusion and acid procedures for the determination of total P in soils and parent materials. The P in the digest was determined by the vanadomolybdophosphoric (VM) yellow colorimetric procedure (Jackson, 1958). This method is well suited for sediment analysis because of its lower sensitivity (1 to 20 ppm of P), color stability, freedom from interferences with a wide range of ionic species up to 1000 ppm and adaptability of HNO_3, HCl, H_2SO_4 and $HClO_4$ systems (Jackson, 1958).

Appropriate aliquots from the original digest (0.500 g in 100 ml) were pipetted into 50 ml volumetric flasks. In order to control the acidity which may vary with aliquot size and carbonate content of the sediment, the pH was adjusted to the 2,6, dinitrophenol colorless end-point (pH 2 colorless - pH 4 yellow). Ten ml of color-forming vanadomolybdate reagent [25 g $(NH_4)_6 Mo_7 O_{24} \cdot 4H_2O$, 1.25 g NH_4VO_3, and 250 ml of concentrated HNO_3 diluted to 1 liter] was added to a 50 ml volumetric flask. The acidity obtained from the combined volumes and reagent concentration was approximately 0.8 N. The acid concentration of the determination is not critical, but the final concentration must be above 0.5 N and not over 1.0 N. The effect of acid concentration on the VM yellow color intensity is shown in Figure 3.7. A plateau is observed in which the color intensity is not affected by acid concentration. The plateau also narrows as the P concentration increases and widens as it decreases. After having allowed at least 20 minutes for full color development, the absorbance was measured by a Beckman DU Spectrophometer at 440 mμ using a blue photocell. This wavelength is suggested by Jackson for working concentrations from 2.0-15 ppm P, which is a typical range obtained from a 5-35 ml aliquot diluted to 50 ml. A light maximum from 400 to 490 mμ is used depending on the sensitivity needed, but ferric

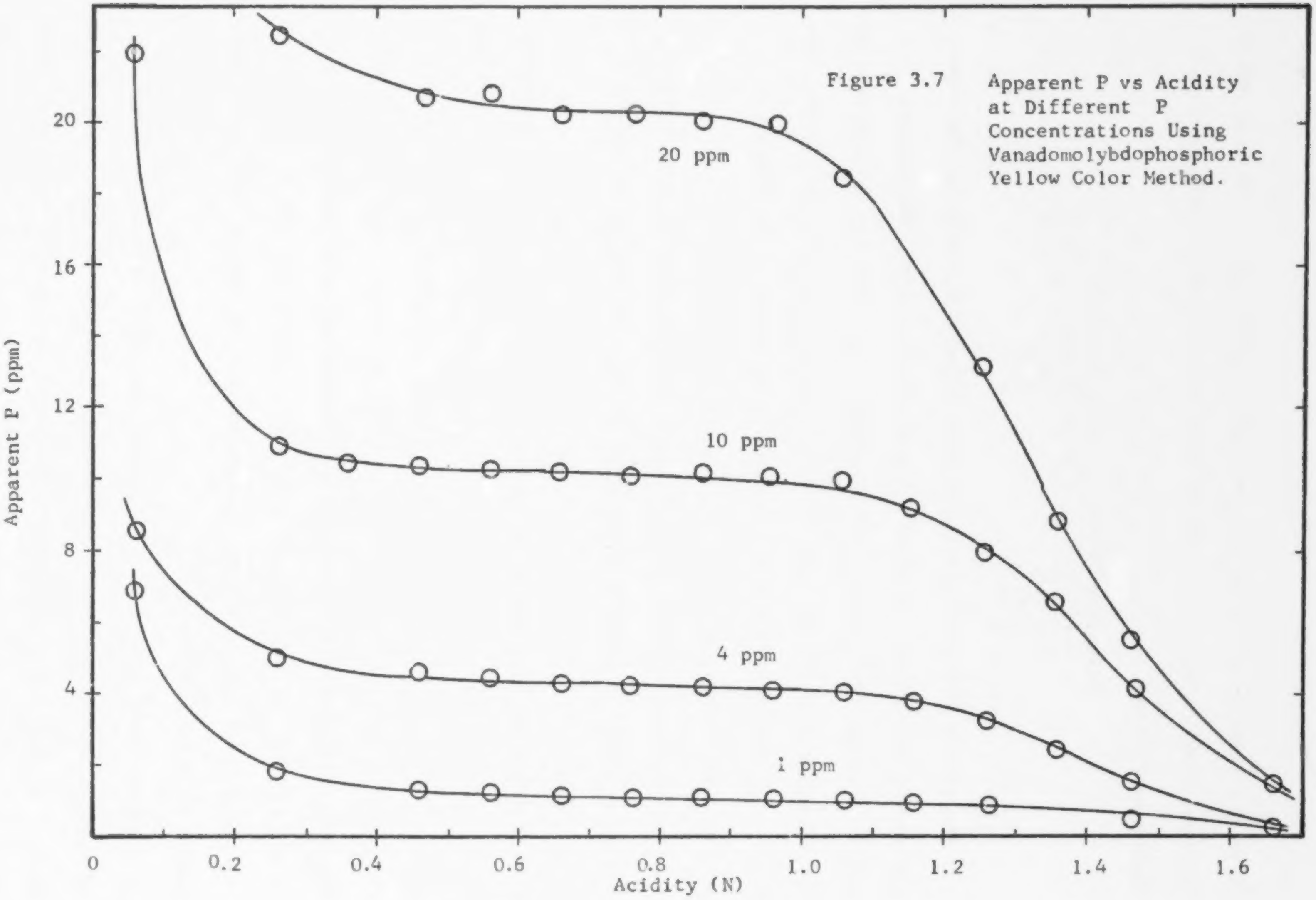


Figure 3.7 Apparent P vs Acidity at Different P Concentrations Using Vanadomolybdophosphoric Yellow Color Method.

ion causes interference with the lower wavelengths, particularly at 400 mμ (Jackson, 1958). Calibration curves were established for different cell lengths as follows:

range, mg P/l	cell length
0.2-2.0	10 cm
0.5-4.0	5 cm
1-10	2 cm
2-20	1 cm

Phosphorus standards and blanks were prepared by carrying the known concentrations through the total P digestion procedure. Experiments showed, however, that the total P standards which were not carried through the procedure measured the same absorbance. This shows within limits, at least, that the VM yellow color complex is not affected by changes in acid and salt concentrations.

Wentz and Lee (1969a) have discussed the sensitivity, minimum detectable concentration, precision and working range for the VM yellow color procedure.

Acid Soluble Phosphorus. This is an operationally defined procedure for extracting P from lake sediments in a 1 N solution of HCl (0.75 N) and H_2SO_4 (0.25 N). Shah et al. (1968) compared the amount of inorganic P extracted by 1N H_2SO_4 (P_a) from a range of New Zealand soils with certain forms of inorganic P determined by a fractionation procedure of Williams et al. (1968). It would appear from their results that the P_a fraction can, as a first approximation, be equated with the sum of acid extractable Ca-P + NH_4F-P + NaOH-P.

Twenty ml of strong acid extractant was added to 0.200 g of sediment in a 50 ml Erlenmeyer flask. The sediment solution was shaken for 15 minutes at 22°C, filtered through a prerinsed 0.45 μ Millipore and diluted to 50 ml. An appropriate aliquot of the filtrate was taken for P analysis using the VM yellow method.

Iron was determined by the orthophenanthroline colorimetric technique (Olson, 1965) or by atomic absorption using a Perkin-Elmer (Model 303) spectrophotometer. Iron standards were prepared ranging from 0.2 to 2.5 ppm and 1.0 to 10.0 ppm for the colorimetric and atomic absorption methods, respectively.

Aluminum, calcium, magnesium, potassium and manganese analyses were determined by atomic absorption. The manufacture's recommended instrument settings and procedures were employed. A nitrous oxide-acetylene flame was used for Al analysis. Appropriate aliquots of the original 100 ml digest solution were taken to make dilutions in the working range of each of the determinations.

Sulfide sulfur was determined by a modified Standard Methods (1965) iodometric titration. Potassium biniodate was substituted for iodine solution and steam stripping of H_2S was used instead of CO_2 stripping. The determination was carried on the AMINCO steam distillation apparatus. Ethanol was added to suppress foaming of acidified carbonate-containing sediments.

Organic Carbon and Carbonate Carbon. For calcareous sediments the analytical problem is to differentiate between the two forms. For the noncalcareous sediments of the northern lakes, total C is considered to be organic C. Total C can be determined by dry combustion as discussed previously. With calcareous sediments, the choice is between determining organic C on the sample after removal of carbonate C or computing organic C by substracting carbonate C from total C. In all quantitative determinations of CO_3-C, the CO_2 released from the carbonates on treatment with acid is measured volumetrically, titrimetrically or gravimetrically. The basic problem is to ensure complete decomposition of the carbonate without hydrolyzing some forms of organic matter by the process of decarboxylation.

A number of methods were evaluated for the determination of organic C and carbonate C in calcareous sediments from Lake Mendota WC-86 as shown in Table 3.3. Only the carbonate C is presented in Table 3.3; organic C can be found by difference from total C. The methods used for each of the determinations are as follows:

1. Acid Neutralization. Samples were acidified with excess 0.5 N HCl, boiled gently to drive out CO_2, then filtered and titrated to the phenolphthalein endpoint with 0.25 N NaOH (Allison and Moodie, 1965). This method of determining carbonate C may be high if other constituents react with acid, or low if constituents (such as Fe) react with base.

2. Soluble Ca from HF-HNO_3-$HClO_4$ Digestion. The Ca dissolved in this acid system would include the carbonates as well as minerals. This method assumes the Ca is present as carbonate and no measureable Ca is bound to the silicate fraction. The Ca measured is converted to CO_3-C equivalents. The assumption that additional Ca in the mineral structures in a high-carbonate sediment (30-80%) would not be a measureable quantity was tested in method 3.

3. Soluble Ca from HNO_3-$HClO_4$ Digestion. This digestion method would dissolve all carbonates + exchangeable Ca + an undefined fraction. The undefined fraction would not include Ca incorporated into the silicate mineral structure. The Ca measured is converted to CO_3-C equivaients. A comparison of method 2 and 3 show less than 10 percent difference throughout the core.

4. Acid Pretreatment. A 50 mg sediment sample (mixed 10:1 with

Table 3.3 Comparison of Carbonate Carbon Determinations on Lake Mendota Core WC-86.

Depth of Core (cm)			Method [a]		
	1	2	3	4	5
			mg CO_3-C/g		
0-5	40.4	31.8	31.8	31.8	48.5 (38)
5-10	36.7	29.4	27.3	28.0	43.0 (38)
10-15	38.2	30.3	28.5	23.9	47.2 (46)
15-20	36.7	28.2	26.7	31.0	42.4 (46)
20-25	37.9	28.2	28.5	27.8	42.3 (46)
25-30	40.7	31.8	31.5	34.5	52.5 (46)
30-35	40.5	31.8	31.8	28.1	43.0 (46)
35-40	41.4	32.7	33.0	38.2	42.7 (46)
40-45	41.0	32.4	33.0	25.1	40.3 (46)
45-50	49.3	39.0	39.3	43.1	48.3 (46)
50-55	60.2	47.7	48.4	63.0	57.5 (46)
55-60	73.7	65.4	60.3	58.5	73.0 (46)
60-65	83.8	76.5	75.0	70.0	87.6 (67)
65-70	81.5	76.5	73.2	69.6	78.1 (67)
70-75	80.2	75.0	72.0	58.0	--
75-80	76.9	71.4	68.5	56.3	72.8 (67)
80-85	75.0	72.0	67.0	67.2	75.9 (96)
85-90	79.0	77.6	73.2	65.0	80.0 (96)
90-95	78.3	75.9	73.9	72.0	83.0 (96)
95-100	77.1	74.8	72.0	63.9	79.0 (96)

[a] Method 1 - Acid neutralization

2 - Soluble Ca from HF-HNO_3-$HClO_4$ digestion

3 - Soluble Ca from HNO_3-$HClO_4$ digestion

4 - Acid treatment prior to dry combustion

5 - LTA -- numbers in parenthesis are hours of LTA

silica) was treated with 0.75 ml of 6 N HCl and 0.25 ml of 5 percent solution of $SnCl_2$ in a vicor crucible. The $SnCl_2$ is used as an antioxidant (Allison and Moodie, 1965). The sample was placed in a heated vacuum desiccator (Precision Scientific Co.) for 7 hours at room temperature and 2 hours at 55°C using full water aspiration for vacuum. The remaining organic matter was determined by dry combustion using the LECO carbon analyzer.

5. Low Temperature Ashing (LTA). Sample ashing was performed in a TracerLab LTA-600 to remove organic carbon (the remaining carbonate C was determined by dry combustion using the LECO carbon analyzer). Oxygen flows into a common inlet manifold, and, at reduced pressure and low flow rate, passes through five separate vertical tubes surrounded by a single radio frequency (r.f.) coil. The r.f. coil generates a high frequency electromagnetic field in which the molecular O_2 is converted to excited, very reactive atomic and ionic species. Volatile products of combustion and excess O_2 are drawn into an exhaust manifold and removed by means of a vacuum pump.

The sample weight in each ceramic combustion boat was 40 mg. The chamber pressure was 1.0 mmHg or less; oxygen flow rate was 65-70 cc/min, and the power to the coil was 240-250 watts. The instrument was not provided with a thermocouple to determine ashing temperature. However, it was expected to be less than 125°C (Personal Communication, Tracer Lab, 1969). The time of ashing varied as shown in Table 3.3. Carbon recovery was checked after LTA using various glucose and $CaCO_3$ ratios. The LTA removes organic carbon effectively in the presence of $CaCO_3$ in a pure system as shown in Table 3.4.

The standard deviation for each of the methods given is shown in Table 3.5. The relative standard error is less than 5 percent for all methods. Acid pretreatment and LTA methods gave the highest standard

Table 3.4 Carbon Recovery of $CaCO_3$ and Glucose After Low Temperature Ashing.

Sample	Theoretical C in Sample (mg C/g) glu	Theoretical C in Sample (mg C/g) $CaCO_3$	Carbon after LTA for 48-56 hr (mg C/g)
$CaCO_3$	--	120	119
Glu:$CaCO_3$ 4:1	320	24	27
Glu:$CaCO_3$ 1:4	80	96	99

deviation. The acid pretreatment method has the disadvantage of hydrolyzing some of the organic material upon acidification. Low temperature ashing requires at least 35 hours exposure to the excited O_2 to obtain complete oxidation of the organic material in sediments. The carbonate carbon values in Table 3.3 appear to be high for the LTA method, thus indicating incomplete oxidation of organic carbon. The mineralogy and composition of the sediment could change the acid and base reactions with noncarbonate materials in the acid neutralization procedure.

Methods 2 and 3 were used in this study to determine CO_3-C for the lakes in southern Wisconsin which contain 25-80 percent carbonate. The Ca dissolved by HF-HNO_3-$HClO_4$ or HNO_3-$HClO_4$ acid systems was converted to CO_3-C equivalents. From the practical standpoint, the CO_3-C determination by method 2 and 3 are the most rapid and reproducible to perform. A comparison of the two acid systems show no measurable Ca is added by HF treatment. The extent to which dolomite contributes to the carbonate is not known. It has been observed that the Mg profile does not increase in the marl layers like the Ca profile. Therefore, some evidence is given that Mg may be derived mostly from other mineral sources. However, a

Table 3.5 Precision of Carbonate Carbon Determinations on Lake Mendota WC-86.

Method	Section (cm)	Analysis	Replicates	Mean (mg/g)	σ	e
1 - Acid neutralization	35-40	CO_3-C	3	41.4	± 0.3	0.7
	80-85	CO_3-C	5	75.0	± 0.3	0.4
2 - Soluble Ca from HF-HNO_3-$HClO_4$ digestion	35-40	Ca	5	109	± 1.1	1.1
	70-75	Ca	5	250	± 0.7	0.2
3 - Soluble Ca from HNO_3-$HClO_4$ digestion	35-40	Ca	5	110	± 0.9	0.8
	70-75	Ca	5	241	± 2.5	1.0
4 - Acid pretreatment prior to combustion	10-15	Org-C	5	68.5	± 1.0	1.4
5 - Low temperature ashing	85-90	CO_3-C	5	79.9	± 2.9	3.6

σ - standard deviation

e - relative standard error = $\frac{\sigma}{\text{mean}} \times 100$

certain percentage of any dolomite would be accounted for in the soluble Ca method. Turekian (1940) used a similar method to determine the carbonate content of deep sea cores. The Ca and Mg were dissolved in 6 N HCl, measured by EDTA titration and converted to $CaCO_3$ equivalents.

Pollen Analysis

Processing Lake Sediments for Pollen Analysis. Chemical treatment of sediments with both mineral and organic fractions consists of demineralization and solubilization and/or chemical conversion of residual organic matter to soluble products. The steps consist of removal of carbonates with HCl, silicates with HF, solublization of humic material with KOH and removal of cellulose with acetolysis solution. Aqueous alkaline solutions are used to eliminate the large lignin-humus fraction of the sediments. The dark-brown humic compounds are then washed free from the sample. The acetolysis solution consists of concentrated H_2SO_4 to bring about the depolymerization of cellulose structures and acetic anhydride to convert cellulose to cellulose triacetate. Cellulose triacetate is not soluble in water but is soluble in glacial acetic acid. The following procedure was used for processing the lake sediment for pollen analysis as modified from Faegri and Iverson (1950), Anderson (1960), and Maher (1969):

1. Weigh 0.200 g of sediment (100 mesh, dried 105°C) in 100 ml beaker. If sediment is calcareous, add 10-15 ml of 10% HCl; heat gently. Add acid until effervescence stops.

2. Add 0.20 ml of internal standard (1 g of eucalyptus pollen in 500 ml tertiary butyl alcohol). Stir with magnetic stirrer for 10-15 min to suspend pollen before pipetting and adjust temperature of internal standard to 27.5°C ± 0.5°C before pipetting.

3. Swirl the sample and transfer to 12 ml centrifuge tube; centrifuge immediately, decant, wash with water, stir, centrifuge and decant. The centrifuge used was International Clinical (Model CL).

4. Transfer sample to same 100 ml beaker and add 15-20 ml of 10% KOH. Boil mixture gently on hot plate for 10 min and stir to prevent bumping. Transfer to 12 ml centrifuge tube, centrifuge and decant (check that solution is not turbid). Wash with water, stir, centrifuge and decant. Repeat if necessary until supernatant water is fairly clear.

5. Transfer sample with 10-15 ml 48% HF to 100 ml teflon beakers. Boil gently on hot plate in fume hood for 3 to 5 min (up to 10 min), then cool and transfer sample to 12 ml centrifuge tube. Wash residue from beaker with a fine jet of water, centrifuge and decant. If a white precipitate (CaF_2) occurs, add 5-10 ml 10% HCl and heat to boiling; immediately centrifuge and decant. Wash with water, stir, centrifuge and decant.

6. Wash with approximately 5 ml of glacial acetic acid, stir, centrifuge and decant.

7. Add 5 ml acetolysis solution (make fresh each lab period by adding 1 part concentrated H_2SO_4 to 9 parts acetic anhydride in a small graduated cylinder). Place tube in boiling water bath for 5 min. Remove immediately, centrifuge and decant. Add 5 ml glacial acetic acid, stir, centrifuge and decant.

8. Add 10 ml tertiary butyl alcohol, stir, centrifuge and decant. Add 5 ml tertiary butyl alcohol, stir, centrifuge and decant. Repeat if desired.

9. Add about 1.5 ml tertiary butyl alcohol, stir and pour concentrate into a 2.5 ml shell vial and flush tube with a fine jet of tertiary butyl alcohol. Place shell vial into the centrifuge tube, centrifuge and decant.

10. Add enough silicone fluid (2,000 cs) to cover the pollen residue (more can be added later), and allow the uncorked vial to stand overnight in a dust-free environment to let the solvent alcohol evaporate. Cork and label.

Counting Ragweed Grains. The prepared sediment sample was diluted with additional silicone fluid and stirred well with a toothpick before mounting on a glass slide. Identification of "Ambrosia-type" pollen were made with high power magnification using a Bausch & Lomb microscope. No reference was given to a particular species of ragweed. The eucalyptus pollen were easily identifiable triangular-shaped grains. Continuous sweeps were made across the entire width of the preparation. The cover slide during the counting was often tapped to turn or move grains to facilitate their identification. In each sample 100 to 200 grains were counted.

Leaching Studies

Aeration Experiment. Samples of wet mud were placed in Pyrex vessels containing 20 l of distilled water. Laboratory compressed air was passed through cotton packing and a water trap, then into the bottom of each vessel through an air diffuser. The air was bubbled at a rate sufficient to keep the sediment in partial suspension throughout the experiment. A magnetic stirrer with a teflon coated bar was also used to maintain constant mixing. The vessels were also covered to keep out the light.

Sample aliquots (350 ml) were removed by a siphon tube located at the midsection of the vessel. Before and during siphoning the entire water-sediment mass was throughly mixed with a long glass stirring rod to ensure that a constant solid to solution ratio was maintained after each sampling.

The samples were centrifuged at 1800 r.p.m. for 20 minutes. Conductance, pH and $(NO_3^- + NO_2^- + NH_3)$-N were determined on the supernatant. The leachate was filtered through a prerinsed 0.45 μ Millipore filter, then soluble P and alkalinity were determined.

(Ammonium + Nitrate + Nitrite)-N was determined with steam distillation in the presence of MgO and Devarda alloy (Al, Zn, Cu) followed by titration with 0.002 N HCl. Devarda alloy is used to reduce NO_3^- and NO_2^- to ammonia which is liberated by steam and collected in boric acid-indicator solution (Bremner, 1965). This method of steam distillation is not affected by various organic and inorganic substances which interfere with colorimetric methods of determining ammonium, nitrate and nitrite. An attempt was made to determine separately ammonia by nesslerization (Standard Methods, 1965) and nitrate by the modified brucine procedure (Jenkins and Medsker, 1964), but difficulty was encountered because of apparent interferences. The accuracy and specifity of the MgO-Devarda alloy methods for ammonia N liberation in the presence of NO_2, NO_3^-, NH_3 and organic compounds is illustrated by Bremner (1965).

Soluble P was determined by filtering the sample through a 0.45 μ Millipore and determining P by the molybdenum blue method using $SnCl_2$ reducing agent (Standard Methods, 1965).

pH was determined with a Beckman Electromate (Model 1009) or a Expandomatic (Model 76) pH meter with a Beckman combination electrode.

Conductance was determined with a YSI (Model 31) conductivity bridge.

Adsorption and Desorption of Inorganic P on Sediments

The method followed was that of Williams et al. (1970) with various modifications. Oven-dried sediment (0.400 g) was placed in tared 50 ml, round-bottom, centrifuge tubes. Twenty ml of 0.2 N NaCl containing 0, 10,

Table 3.6 Mean, Standard Deviation and Relative Standard Error for Chemical Analysis of a Calcareous and Noncalcareous Lake.

Analysis	N	Wingra (WC-92)			Trout, N. (WC-60)		
		$\bar{x}$	σ	e	$\bar{x}$	σ	e
Total-C	5	128	7.0	5.5	145	4.9	3.4
		168	8.6	5.1	220	5.3	2.4
Org-N	5	7.08	0.36	5.1	---		
NH_4-N	5	0.073	0.009	12	---		
		0.21	0.014	6.7			
		0.20	0.040	20			
P	5	0.538	0.0032	0.59	2.15	0.035	1.6
		0.507	0.006	1.1	1.44	0.022	1.5
		0.742	0.081	1.1			
Acid sol-P	5	0.284	0.0010	0.35	---		
		0.646	0.0087	1.34	---		
Fe	5	8.04	0.20	2.5	46.3	5.9	12.8
		7.96	0.33	4.1	36.7	1.9	5.2
		2.00	0.78	3.9			
Mn	5	0.562	0.0	0.0	1.72	0.025	1.5
		0.622	0.012	1.9	1.12	0.011	1.0
		0.276	0.0	0.0			
Ca	5	233	4.4	1.9	2.32	0.13	5.6
		318	8.0	2.5	3.61	0.21	5.8
Mg	5	10.2	0.22	2.2	3.32	0.32	9.6
		9.10	0.22	2.4	4.03	0.23	5.7
		6.02	0.59	9.8			
K	5	5.67	0.13	2.3	4.12	0.099	2.4
		5.45	0.03	5.5	5.41	0.20	3.7
		0.53	0.059	11			
Al	5	31.3	0.28	0.90	23.5	0.29	1.2
		30.5	0.21	0.69	31.4	0.22	0.7
		8.2	0.17	2.1			

N = replicates

$\bar{x}$ = mean

σ = standard deviation, N-1 degrees of freedom

e = relative standard error = $\frac{\sigma}{\bar{x}} \times 100$

20, 50 and 100 μgP/ml (KH_2PO_4) and 20 ml of distilled water were added to make the water to sediment ratio 100:1. The sample tubes were agitated on a Burrell wrist-action shaker for 40 ± 4 hours at ambient temperature (28-29°C) centrifuged for 20 minutes at 2400 r.p.m. and filtered through a 0.45 μ Millipore to remove final turbidity. A 0.1 N NaCl system was used to facilitate particle setting during centrifugation. After the supernatant was removed the tubes were reweighed to determine the amount of P entrapped in the residue. The correction for P entrapped in the residue was applied to the subsequent desorption step. The P desorption step involved adding 40 ml of 0.1 N NaCl, shaking the solution for 40 hours, centrifuging and filtering as described previously. A control sample was run to determine the P released from the sediment to which no P was added. Phosphorus was determined by the VM yellow or the molybdate blue method depending on the concentration of P added to the sediment and the adsorption or desorption capacity of the sediment. The pH of the centrifuged solution was determined by a combination electrode after the adsorption and desorption steps. Duplicate runs were made on each sediment.

D. Statistical Evaluation of Analysis

The results presented in Appendix I for the chemical analyses of each core are mean values of two or five replicate determinations. A standard deviation was calculated for each of the 5 replicate determinations and presented in Appendix I with the chemical data. The standard deviation, mean and relative standard error for the measured parameters of a typical calcareous and noncalcareous lake are shown in Table 3.6 for Lake Wingra and North Trout Lake, respectively. The relative standard error was less than 5 and 10 percent for 66 and 25 percent of the analyses, respectively. The relative standard error for exchangeable ammonium ranged from 6.7 to 20 percent. A precision and accuracy determination on a Florida phosphate rock obtained from the National Bureau of Standards of the U.S. Department of Commerce was presented by Bortleson (1968).

Duplicate pollen counts were made from each processed sample. In the transition zone (high to low ragweed) triplicate counts were made. Ten replicate counts were conducted on Lake Monona (WC-101) and Devils Lake core section number 13 and 1, respectively. The mean ragweed pollen counts and standard deviation were 39 ± 5 and 43 ± 7 for Lake Monona and Devils Lake, respectively.

The results presented for the leaching of P and N and sorption desorption of P studies represent the mean value for duplicate determinations.

IV. EXPERIMENTAL RESULTS

The experimental results from this investigation may be separated into the following phases: 1) identification of the pre- and postcultural deposits in the sedimentary column using Ambrosia (ragweed) pollen as an indicator, 2) determination of the chemical stratigraphy of hard-water lakes, Mendota, Monona and Wingra in southern Wisconsin, 3) determination of the chemical stratigraphy of soft-water lakes, Little St. Germain, Trout, Minocqua, Little John and Weber in northern Wisconsin and Devils in southern Wisconsin, 4) estimation of recent sedimentation rates using the sedimentary depth of Ambrosia pollen and historical records of the Wisconsin settlement era, 5) determination of sedimentation intensity of chemical components in the postcultural sediment using estimates on sedimentation rates and dry solids content in core profiles, 6) determination of leaching potential of inorganic N and P from Lake Mendota pre- and postcultural sediment and 7) determination of the sorptive-desorptive capacity of P on selected sediment levels of pre- and postcultural sediments.

The results of the core analyses are presented in Appendix I. The tabulated data are mean values of two or five replicate determinations for each core interval. A standard deviation is calculated for each of the 5 replicate determinations.

A. Identification of Pre- and Postcultural Sediments Using Ambrosia Pollen

Cores were taken from the upper 50-100 cm of sediment for most of the lakes examined; this depth of accumulation was sufficient to include deposits representing the presettlement period in Wisconsin. In order to identify pre- and postcultural periods of deposition in the core column, Ambrosia (ragweed) pollen counts were performed, and the results were interpreted with respect to historically known changes in vegetation, including early settlement, lumbering and farming.

Ragweed occurs in relatively high percentages (5-40%) in surface sediment samples from the deciduous forest region of the northeastern and northcentral U.S.A.; the plant seems to have increased as a result of disturbance and creation of open habitats through forest clearance by European settlers (Ogden 1967; Davis, 1967; Wright, 1968). A short core (50 cm) was taken from Frains Lake in Michigan by Davis (1968). From its pollen content, sediment deposited at the time of land settlement and forest clearance was identified. The change in vegetative cover resulted in a sharp decline in tree pollen, especially oak, and a sudden relative increase in pollen from weedy herbs. Ragweed pollen was especially affected, increasing from less than 1 percent to about 30 percent of the total. Many profiles of small lake and bog sediments in or near the Great Lakes drainage basin show a similar sharp increase in the relative abundance of Ambrosia pollen near the tops of cores (Ogden, 1966).

In Table 4.1 and 4.2 are shown the ragweed pollen counts with depth of sediment for the noncalcareous and calcareous lakes, respectively. The base of the cultural horizon in the cores is indicated by the appearance and rapid build up to relatively high levels of Ambrosia ragweed pollen. The appearance of these pollen grains provides a stratigraphic horizon which can be dated from historical records showing when man moved into the region and began modifying the ecology. A later discussion will detail the use of Ambrosia pollen for estimating

Table 4.1 *Ambrosia* Pollen with Sediment Depth for Noncalcareous Wisconsin Lakes.

Depth of Sediment (cm)	Trout, N.	Trout, S.	Minocqua, N.W.	Minocqua, S.W.	Little St. Germain, W.	Little St. Germain, S.	Little John	Sparkling	Weber	Devils
	Ragweed Pollen/100 Eucalyptus Pollen (Eu)									
0-5	59	29	44	37	39	32	36	63	74	46
5-10	36	27	29	42	38	32	36	66	67	43
10-15	52	28	28*	27	34	32	41	45*	37	34*
15-20	63	43	15	24	29	32	56	20	34*	19
20-25	33	38	14	20	29	40	46	17	21	13
25-30	36 *	31	11	16*	26	34	50	20	22	10
30-35	18	22	13	7	26	39	45	22	19	17
35-40	15	17*	14	4	27*	32	42	14	20	14
40-45	4	3			11	18*	21*	16	17	19
45-50	9	2	20	5	6	10	9	9	21	7
50-55	14	n.d.	16	3	6	8	8	10	12	9
55-60	n.d.	1		6	n.d.	12	11	13	17	16
60-65	8	1		4	3	12	9	15	18	15
65-70	n.d.	n.d.		4	n.d.	8	10	19	15	10
70-75	5	0			9	2	n.d.	12	21	6
75-80	n.d.	n.d.			n.d.	2	13	4	19	12
80-85	14	0			6	1	n.d.	5	22	6
85-90					5		10	16	17	9
Water depth(m)	26	33.2	10.7	13.7	15.6	7	5	18.8	12.6	13.1
Mean ragweed for postcultural period	46	29	34	28	31	32	42	60	53	41
Mean ragweed for precultural period	11	1	15	5	7	7	10	14	19	12

* Horizon showing rise in ragweed pollen

No determination = n.d.

Table 4.2 *Ambrosia* Pollen with Sediment Depth for Calcareous Southern Wisconsin Lakes.

Depth of Sediment (cm)	Wingra	Monona WC-101	Monona WC-46	Mendota WC-89	Mendota WC-86	Mendota WC-84	Mendota WC-82
	Ragweed Pollen/100 Eucalyptus Pollen (Eu)						
0-5	30	38	38	28	56	24	4
5-10	22	42	27	42	55	28	3
10-15	23	34	31	30	58	30	2
15-20	28	31	23	32	47	31	1
20-25	28	33	27	33	36	31	4
25-30	20	21	28	26	34	28	n.d.
30-35	19	26	27	24	41	33	0
35-40	20	28	25	14*	26	28	0
40-45	25	23	28	3	18 *	39	0
45-50	21	25	17	4	14	21 *	1
50-55	30	23	13 *	2	4	14	0
55-60	17	25	4	4	4	10	n.d.
60-65	20	39	2	n.d.	n.d.	7	2
65-70	14 *	34	n.d.	2	0	3	n.d.
70-75	2	21	5	2	n.d.	7	2
75-80	2	22	n.d.	5	7	7	n.d.
80-85	5	14	3	n.d.	n.d.	8	1
85-90	6	18	3	n.d.	5	4	n.d.
90-95	-	15	2	n.d.	n.d.	4	1
Water depth (m)	3	21	15.9	23.2	18.3	11.8	3.8
Mean ragweed for postcultural period	23	--	26	29	42	29	--
Mean ragweed for precultural period	4	--	3	3	7	7	--

* Horizon showing rise in ragweed pollen

No determination = n.d.

the postcultural sedimentation rate. The horizon showing a marked increase in ragweed abundance varies considerably between lakes. The profiles of South Bay of Little St. Germain and Little John show a rapid increase in ragweed at a depth of 40-45 cm. On the other hand, the marked increase in ragweed abundance is found at the 10-15 cm level, in the northwest bay of Minocqua, Sparkling and Devils lakes. The change from low to high ragweed counts is deeper in the column for calcareous than noncalcareous lakes. The thickness of the unconsolidated sediments produced during the postcultural interval may vary depending on the rate of sediment accumulation, the moisture content, core compaction or grain size of the sediments. For instance, in the noncalcareous lakes the sediments are less consolidated and have a higher moisture content than the calcareous sediment. Thus, the thickness of the postcultural wet sediment column in the noncalcareous lakes is often about the same thickness as the calcareous lakes even though the latter sediments are accumulating much faster based on dry solids content. In all lake cores examined, a low count of ragweed appears in precultural sediments, and the increase in ragweed pollen in the upper part of the cores changes rather abruptly, usually over a 5 cm interval. The mean ragweed count for the postcultural sediment is about 4-6 times greater in the postcultural than the precultural sediment for most lakes investigated. If the surface sediments were mixed appreciably, then such comparisons would be invalidated. However, it must be concluded that the fairly abrupt profile changes in ragweed pollen suggest the depth of mixing does not appreciably influence the stratigraphy of the deposit. Where the transition zone from low to high ragweed counts is more gradual, the estimate on the horizon separating the pre- and postcultural sediment is less accurate.

B. Chemical Stratigraphy of Calcareous Lakes in Southern Wisconsin

Lake Mendota

Surface Sediments. Surface sediments from 32 stations were collected by Ekman dredge from Lake Mendota by Delfino (1968) and were analyzed for P, Fe, Mn, Mg, K, Na and Ca (Delfino, Bortleson and Lee, 1969). The purpose of this sampling was to assess the chemical composition of the sediments with respect to water depth and location within the lake. As an aid in the interpretation of the analytical data, statistical analyses were applied which compared the elemental concentration (mg/g dry weight basis) with depth of sample recovery. The elemental analysis of Lake Mendota surface sediment and the statistical correlation data are shown in Table 4.3 and 4.4, respectively.

Manganese, Fe and P show a positive statistical correlation between concentration and sample depth. For example, the highest concentration of total P is 1.8 mg/g from the deepest part of Lake Mendota and the concentration of P decreases by about one-half of the above amount in the shallower areas in the lake. A significant inverse correlation is found for Mg and K. Statistical correlation does not necessarily imply causation so that water depth and morphology need not be the primary controlling factors bearing on elemental concentrations in the sediments. Other unmeasured or unidentified variables could be in operation and these might just as easily be responsible factors for the findings reported (Delfino et al., 1969).

The occurrence of fine particle settling could explain the correlations found in this work. Since higher concentrations of Mn, Fe, and

Table 4.3 Lake Mendota Surface Sediment Data [After Deifino, Bortleson and Lee (1969)].

Sample number[a]	Depth of recovery, meters	Date of recovery, 1967	Mg./G.[b]						
			Manganese	Total iron	Total phosphorus	Total magnesium	Total potassium	Total sodium	Total calcium
1	22	June 12	1.34	22.4	1.35	12.5	12.5	14.2	108
1	22	June 19	1.33	22.8	1.35	13.2	12.5	14.6	111
1	22	June 21	1.32	22.8	1.38	13.5	12.7	14.9	111
1	22	June 22	1.32	23.6	1.38	13.4	12.5	14.7	111
2	19	June 12	1.19	21.2	1.29	17.0	13.0	15.5	112
3	15	June 12	0.90	19.1	0.85	17.8	12.5	15.6	114
4	12	June 14	1.22	23.0	1.30	14.9	15.0	16.5	114
5	9	June 14	0.76	20.8	0.92	15.3	14.3	16.7	100
6	18	June 14	1.19	24.2	1.45	13.2	13.0	15.1	105
7	9	June 15	0.64	21.2	0.89	15.7	14.7	16.4	80
8	17	June 15	1.22	21.4	1.29	14.0	12.0	14.8	114
9	22	June 19	1.26	24.4	1.45	11.6	12.3	15.0	112
10	15	June 19	1.11	22.3	1.01	15.9	10.5	16.4	108
11	9	June 19	0.76	20.8	0.89	16.4	12.3	16.6	125
12	10	June 19	0.90	16.0	0.84	26.0	26.0	13.6	80
13	23	June 21	1.40	25.6	1.35	13.0	12.5	14.6	103
14	10	June 21	1.04	19.5	1.17	15.2	11.5	14.6	117
15	12	June 21	1.11	20.8	1.02	12.7	12.2	14.4	90
16	21	June 21	1.12	24.8	1.42	12.3	12.2	14.3	97
17	21	June 22	1.34	25.2	1.38	11.8	12.2	...	90
18	19	June 22	1.17	24.4	1.42	12.8	13.5	...	89
19	23	June 26	1.30	23.4	1.47	13.0	12.2	15.1	99
20	23	June 28	1.34	23.4	1.53	16.0	12.0	14.7	100
21	22	June 28	1.20	23.2	1.37	12.1	12.0	18.4	98
22	21	July 5	1.18	25.0	1.62	11.1	13.1	14.2	78
23	20	July 5	1.34	25.0	1.52	12.6	13.8	15.0	88
24	21	July 5	1.04	24.8	1.22	10.9	12.3	15.2	97
25	18	July 6	1.14	21.2	1.20	...	...	...	...
26	18	July 6	1.15	21.4	1.25	13.7	11.8	15.1	113
27	18	July 6	1.15	22.3	1.26	12.9	12.5	16.4	120
28	23	July 12	1.32	24.0	1.50	11.4	12.3	16.8	109
29	18	July 12	1.00	21.2	1.09	14.6	12.3	15.5	109
30	19	July 12	1.00	23.0	1.15	11.8	12.0	15.8	106
31	23	Oct. 11	1.43	22.8	1.41	13.0	11.8	15.0	124
32	24	Nov. 6	1.50	26.7	1.82	12.2	12.2	15.0	112

[a] Samples 1–30 were collected during summer thermal stratification. Samples 31 and 32 were collected during the fall circulation period.
[b] Oven-dry weight (105° C.) basis.

Table 4.4 Statistical Correlation Data for Relationship between Depth of Sample Recovery and Element Concentration in Lake Mendota.

Element	r[a]	p[b]	s[c]	n[d]
Manganese	0.81	0.001	0.13	30
Iron	0.74	0.001	0.98	30
Phosphorus	0.82	0.001	0.22	30
Magnesium	-0.59	0.025	2.29	29
Potassium	-0.40	0.025	2.34	29
Sodium	-0.15	e	f	27
Calcium	0.04	e	f	29

[a] Linear correlation coefficient

[b] Significance level of correlation

[c] Standard error of estimate

[d] Degrees of freedom, n = N - 2

[e] Not significant

[f] Not computed

P are found at deeper depths in Lake Mendota and since these deeper depths are essentially in the middle or central part of the lake, a relatively simple particle fractionation of tributary-borne suspended matter may have occurred. Particle size analyses of the sediment samples were not conducted so that conclusive evidence is lacking. However, four cores taken from Lake Mendota in progressively deeper water show a percent solids decrease with increasing depth as shown in Figure 4.1. This would indicate that there is a natural grading process occurring in the lake during which finer solids are settling in the deeper zones. Delfino and Lee (1968) reported that essentially all of the Mn in Lake Mendota waters is soluble and passed through either 0.45, 0.22 or 0.10 µ pore size membrane filters. Thus, any residual suspended particulate Mn would have to be on the order of less than 0.10 µ in diameter. This fact would require the suspended material and its associated elements to be present in a very small colloidal form.

This interpretation is supported by studies of annual pollen deposition per unit area measured in sediment traps at Frains Lake in Michigan by Davis (1968). At Frains the ratio of deposition, as measured in traps, to net accumulation, as measured in sediment cores, showed the pollen grains were deposited an average of two to four times before being buried deeply enough to escape further disturbance. Davis (1968) explained that the sediments in shallow water were apparently stirred up and resuspended more frequently or more extensively than sediment in deep water; the net result of repeated resuspension mainly from shallow water sediment, followed by redeposition over the entire basis, was movement of material from shallow to deep water. Nichols

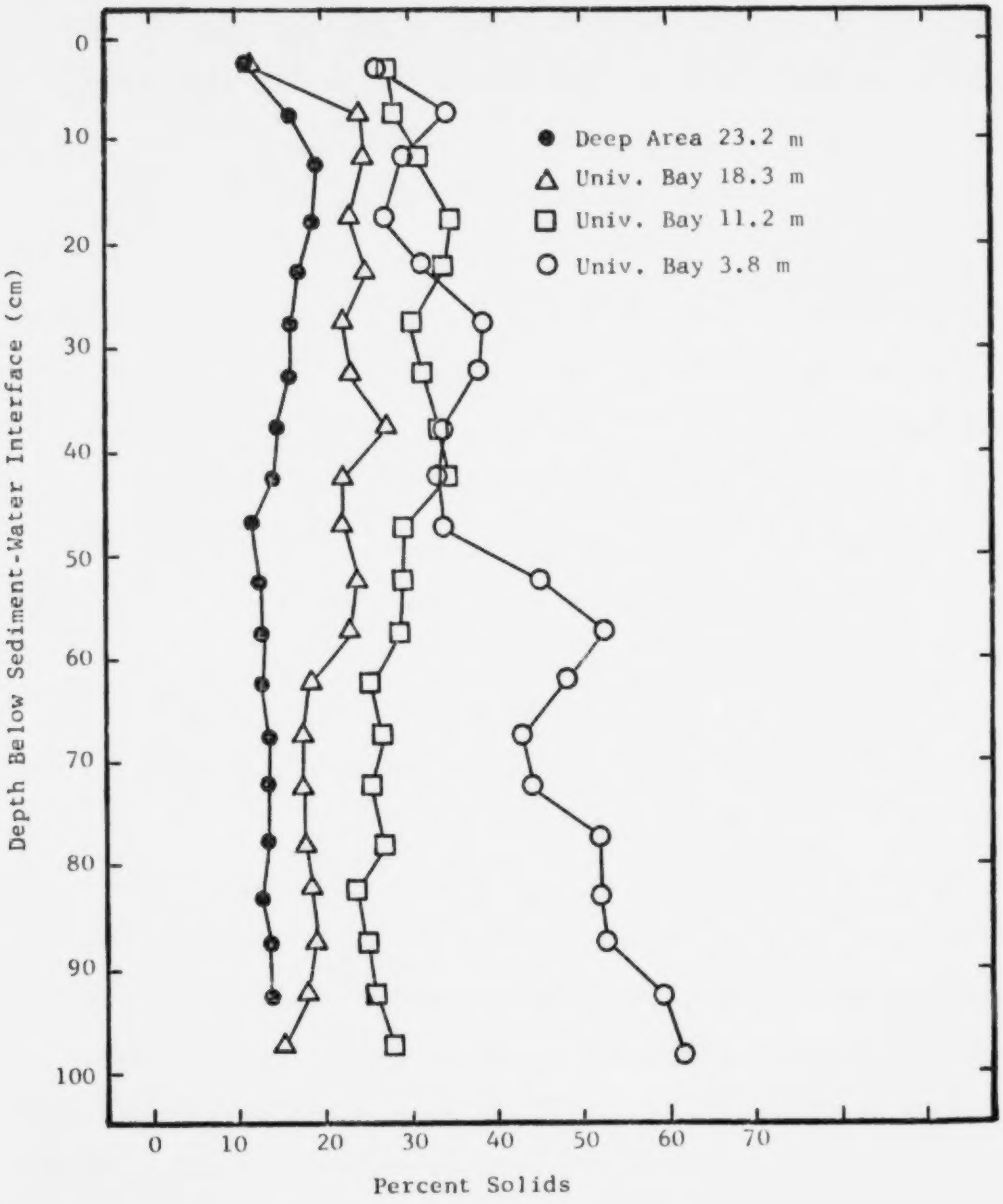


Figure 4.1 Percent Solids (Dry Weight) with Depth of Sediment in Lake Mendota Cores.

et al. (1946) noted that copper sulfate applied to the bay areas of Lake Monona (1925-1944) was recovered in highest concentrations in the deep portions of the lake. It seems that the natural grading process carried the precipitated Cu compounds to the deeper waters. Frink (1967) collected bottom samples from Bantam Lake, Conn., and found that total P and N increased with water depth. The sediments in the deeper water of Bantam Lake contained more P and an increasing proportion of this P was readily exchangeable (Frink, 1967).

Reproducibility of Phosphorus Stratigraphy. If it is assumed that cores taken from the deep area of Lake Mendota are more nearly representative of the depositional processes occurring over the entire basin, it then becomes important to know the reproducibility of the distribution patterns for cores within the central area of the lake. Four cores, approximately 75 cm long, were taken in 21.2 m of water in the deep area of Lake Mendota over the ice 12-15 feet apart on the same day in February, 1969. Phosphorus was chosen as the element to use to study the variations in the core column because of the accuracy, precision and other analytical attributes of the vanadomolybdate method for P (Wentz and Lee, 1969a; Jackson; 1958).

The phosphorus profiles for replicate Lake Mendota cores IR-IVR are shown in Figure 4.2 and 4.3 for 5 cm (2), 2 cm and 8 cm intervals. The results indicate the basic P profile is reproduced for each core taken at the same site, and the P profile compares well with the deep-water core, WC-89 (not shown) taken in 1966. The concentrations of P for the replicate cores are nearly the same, and maximum P concentrations are at the surface level and at a level below the surface sediment.

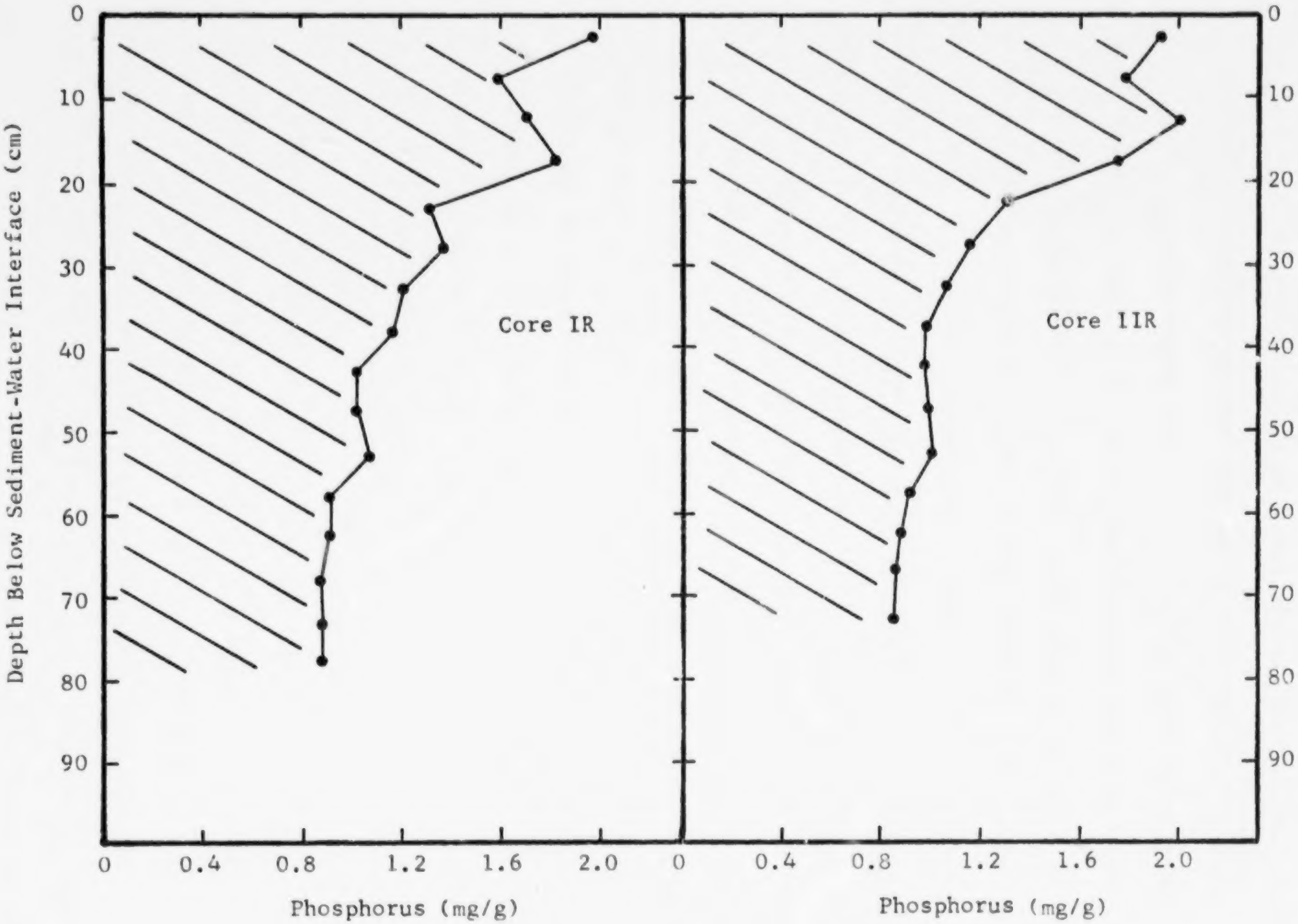


Figure 4.2 Phosphorus Stratigraphy of Deep-Water Lake Mendota Cores Fractionated into 5 cm Intervals.

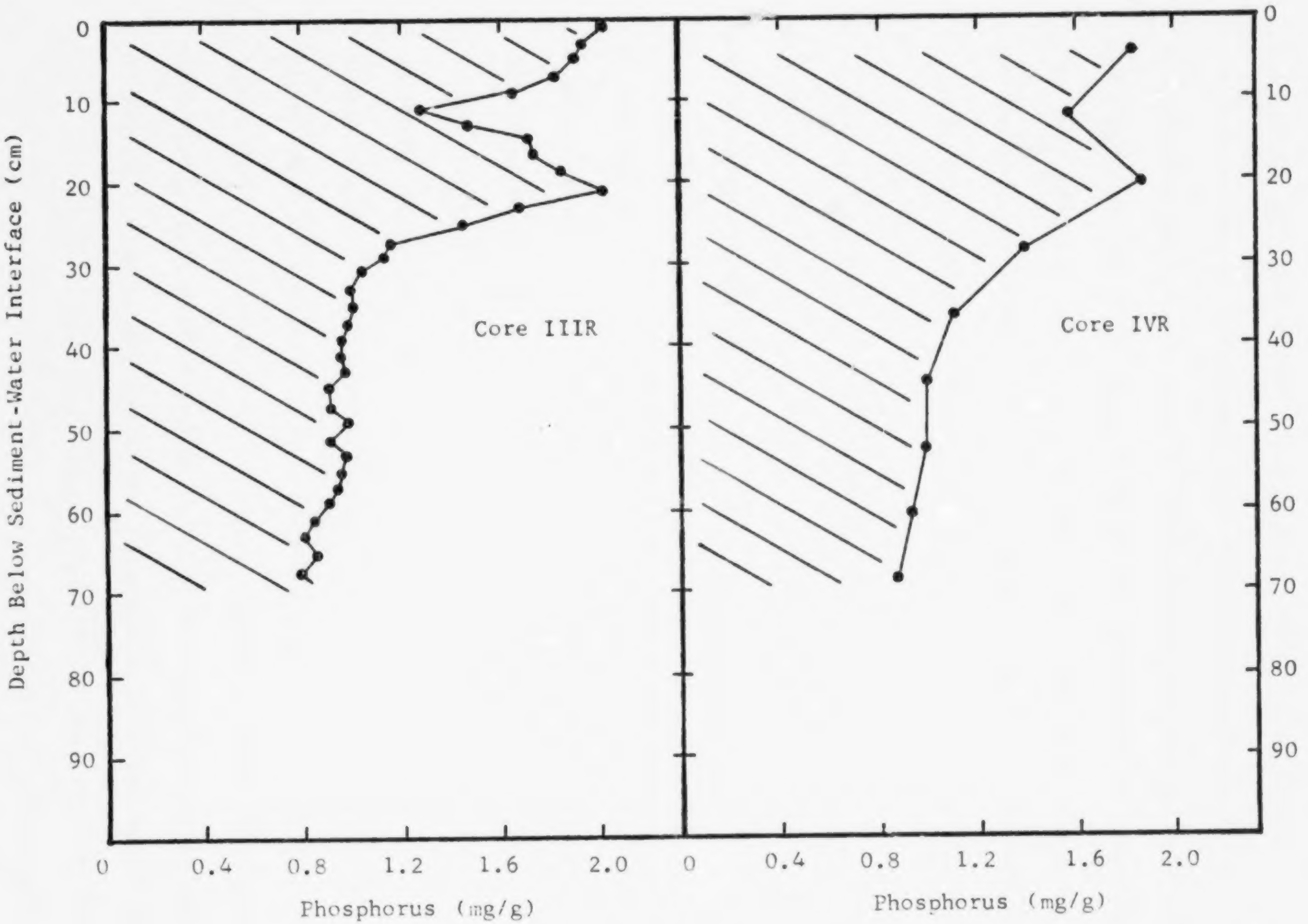


Figure 4.3 Phosphorus Stratigraphy of Deep-Water Lake Mendota Cores Fractionated into 2 cm Intervals (IIIR) and 8 cm Intervals (IVR).

Too much reliability cannot be placed on the exact level of a fluctuating pattern in a core, since the maximum P shifts from the 10-15 cm stratum to the 15-20 cm stratum. These changes may be due in part to the imprecise nature of fractionating the core and to real differences that may exist in the layers of sediment in the lake bottom. Replicate cores taken may be compacted or expanded differently when the core is cut and when the core is extruded. Errors may also exist in obtaining the interval sizes fractionated at the same point in replicate core columns.

As shown in Figure 4.2, the profiles for cores IR and IIR which were fractionated into 5 cm intervals exhibit a slight difference in the position of the maximum peak. In core IIIR, which was fractionated into 2 cm intervals, the two maximum peaks become more pronounced as shown in Figure 4.3. Undoubtedly, core IIIR taken in 2 cm intervals could be interpreted with greater confidence than the other cores. As shown in Figure 4.3, the P profile of core IVR fractionated into 8 cm intervals shows a further smoothing out of the slight variations found in the other cores, as might be expected with larger size intervals. However, the two maximum peaks are still retained in core IVR. It would appear that the general interpretation of the P distribution with depth would be the same for cores fractionated into 5 cm or 8 cm intervals. However, the interpretation of core IIIR may be slightly different because the variations are more pronounced, indicating that a more dramatic increase of P deposition occurred over a short interval (28-22 cm), whereas the P profiles of the other cores indicate a steady increase of P deposition over a longer interval (35-15 cm). Greater resolution in following chemical sedimentary changes for Lake Mendota is achieved by fractionating into less than 5 cm intervals. If mixing were deeper than only the upper layers (ca. 2-5 cm) in Lake Mendota deep-water sediments, greater resolution would not be observed by taking 2 cm intervals. To achieve the resolution obtained in the 2 cm interval fraction would have involved considerably more analytical work. In this sense, mixing may be advantageous because the resultant integration of old and recent particles make less necessary any effort to analyze more closely spaced intervals. The 5 cm interval size probably represents a compromise on the amount of additional analytical work needed and the amount of resolving detail achieved. Nevertheless, the gradual or abrupt observations in the percentage diagrams are also dependent on the interval size used.

This type of study is of particular importance in light of evidence for the mixing of sediments by burrowing organisms (Ogden, 1967; Davis, 1967) and by density currents (Bryson and Suomi, 1952). Since two maximum peaks and practically the same trends of P deposition are observed in all cores, including core WC-89 taken in 1966, it appears from this study that the solid phase component of sediment in the top layers is not a fluid mass subject to vertical displacement over a short period of time in the deep-water sediments of Lake Mendota. Over a long period, changes may take place in the concentration of P in the upper layers because the depth of vertical mixing or the depth at which a sediment particle is incorporated into the motionless historical layer is not known. Undoubtedly, vertical mixing of sediments by benthonic animals or mechanical agents near the sediment-water interface is occurring, but the extent of mixing does not appear to laterally or vertically change the overall distribution pattern of P in the deep-water area of Lake Mendota.

Deep-Water Profile WC-89. (Note on the digestion procedures used: It should be borne in mind by the reader that the digestion of the sediment samples for Mendota core WC-89, Monona core WC-46 and Trout core WC-59 was done without the preliminary HF treatment; therefore, the concentrations of Al, Mg and K will be a fraction of the total. However there is no detectable difference analytically in the sedimentary concentrations of Fe, P, Mn and Ca using either $HF-HClO_4-HNO_3$ or $HClO_4-HNO_3$ digestion procedures (Bortleson, (1968)). The chemical stratigraphy of Lake Mendota core WC-89, obtained in 23.2 m of water, is given in Figure 4.4. The upper 55 cm of sediment consists of a finely divided, homogeneous, black mud, or gyttja, followed by a 15 cm transition zone to a buff-colored marl, which is dominant in the lower 25-30 cm. Murray (1956) maintained the black color in the gyttja results from the presence of ferrous sulfides deposited under conditions of oxygen deficiency and not from the organic content. Berner (1964) found that recent sediments containing fine-grained black FeS, even in small concentrations, tend to be colored gray and black. Upon addition of HCl or on standing, the sediments show a noticeable color change as the black material decomposes. The black gyttja contains 25-31 percent $CaCO_3$, and the marl contains 47-50 percent $CaCO_3$. The rise in ragweed pollen at the 35-40 cm interval separates the pre-and postcultural sediment. The ragweed horizon is 25 cm above the gyttja-marl boundary, thus it appears the black gyttja was deposited in the center of the

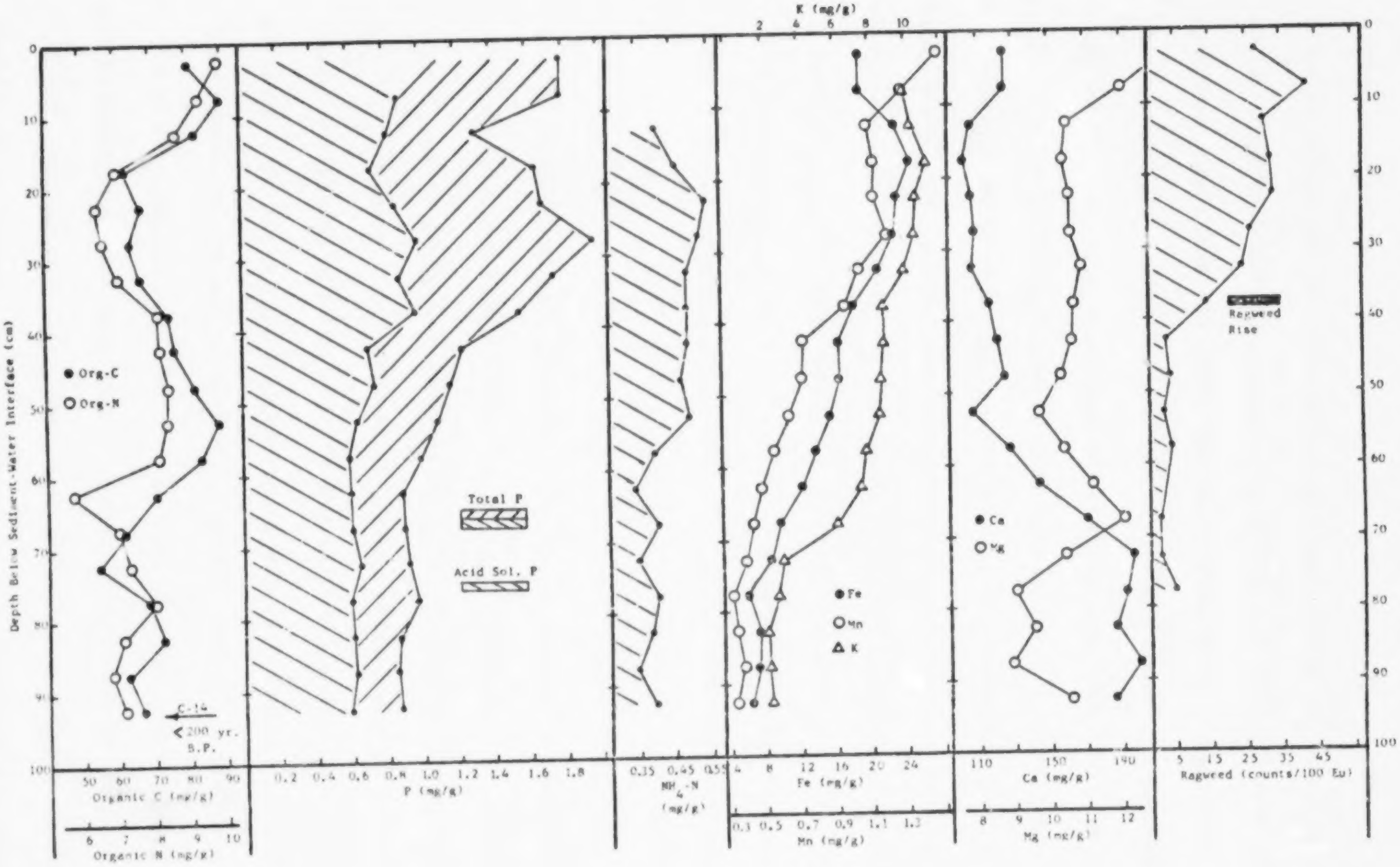


Figure 4.4 Chemical Stratigraphy of Lake Mendota Profile WC-89 [Acid Soluble P Data After Wentz and Lee (1969b) and Mn Data After Delfino (1968)].

lake prior to the major disturbance by man in the Lake Mendota watershed. A radiocarbon age of the organic material at the 90-95 cm interval dates less than 200 years before present (B.P.) according to Bender (1969). However, considerable error may exist for radiocarbon dating of recent sediments (Ogden, 1967). In all the calcareous lake cores, the gyttja, the transition zone between the sediment types as well as the marl are estiablished by the Ca profile or the $CO_3^{=}$-C values.

Organic C and organic N concentrations fluctuate with depth of sediment; however, the mean concentration of organic C and organic N above and below the ragweed horizon is approximately the same. Murray (1956) also noted that the organic content was essentially the same in the gyttja and marl layers. Concentrations of organic C and organic N throughout the core are 54-90 mg/g and 6-10 mg/g, respectively. Maximum concentrations of organic C are observed in both pre- and postcultural sediment.

Exchangeable ammonium N (NH_4^+-N) concentrations are higher in the upper postcultural sediment ranging from 0.41-0.55 mg/g, whereas in the precultural sediment the concentration is 0.34-0.41 mg/g.

The total P concentration remains constant at approximately 0.8-0.9 mg/g within the marl and through the marl-gyttja transition zone (70-60 cm). A gradual increase occurs thereafter (60-25 cm), yielding a range of 1.0-2.0 mg P/g. The maximum peak at the 25-30 cm interval is followed by a decline and rise in P content in the upper 30 cm of sediment. Acid soluble P concentration, as determined and reported by Wentz and Lee (1969 a,b), follows a trend similar to total P. The P released with 0.075 N HCl-H_2SO_4 extractant is an operationally defined fraction of the total which is desorbed at 20°C at pH 1-2 (Wentz and Lee, 1969a). Presumably, the acid extractant would remove Ca-bound forms of P plus an undefined fraction of Fe-P and Al-P. Acid soluble P concentrations are 0.61-0.73 mg/g and 0.72-0.96 mg/g in pre- and postcultural sediment, respectively (Wentz and Lee, 1969b). The ratio of acid soluble P to total P decreases above the 55-60 cm level indicating that the more recent sediment contains a greater fraction of P which is not acid extractable.

Iron, Mn and K increase from a constant background concentration of 7-8 mg/g, 0.4-0.5 mg/g and 2-3 mg/g, respectively, in the marl and gyttja-marl boundary to 2-4 times these concentrations in the postcultural sediments. The initial rise in Fe, Mn and K concentrations at 65-70 cm begins before the appearance of ragweed pollen. The sediment at the 65-70 cm level is estimated to be 165-200 years B.P. based on the rise in ragweed at 100 years B.P. The Fe profile is similar to the distribution pattern for total and acid-soluble Fe found by Nriagu (1967-68) for a Lake Mendota deep-water core. Most of the Fe was soluble in boiling 1N HCl. Nriagu (1967-68) explained that the fraction of acid-soluble Fe which was not tied up as a Fe sulfide was coprecipitated with calcite.

The Mg profile presents no increasing or decreasing trend with depth of sediment.

University Bay Profiles WC-82, -84 and -86. It is not known whether substantial differences can be observed in the horizontal stratification Lake Mendota sediments. The changes in chemical stratigraphy below the sediment-water interface for three cores taken along a transect from the shallow area of University Bay towards the center of the lake are shown in Figure 4.5, 4.6 and 4.7. Profiles WC-82, -84 and -86 were taken in progressively deeper water of 3.8, 11.6 and 18.3 m, respectively.

The horizon showing a marked increase in ragweed pollen is progressively deeper into the sediments for profiles WC-89, -86 and -84, respectively. However, an increase from low to high ragweed counts is not observed for the shallow-water core WC-82. Apparently, the pollen is resuspended in the shallow-water areas and transported to deeper water before final deposition. Since the ragweed pollen rise from low to high counts occurs at greater sediment depth for WC-84 and WC-86 than the deep-water core WC-89, a faster sedimentation rate or a greater mixing depth is implied. For profile WC-84 and WC-86, the ragweed horizon coincides with the top of the gyttja-marl transition zone as shown by the Ca profiles. In core WC-82 the transition from low to high $CaCO_3$ content occurs at the 10-15 cm level. The short column of gyttja indicates the nearness of core WC-82 to shoreline deposits where the normal physiochemical conditions at this location may be greatly modified by vegetation, greater frequency of wind generated currents and other shoreline phenomena. A one meter segment of sediment probably represents a much greater time span than the other cores obtained from University Bay.

There are similarities as well as differences in the organic C distribution patterns of the University Bay cores and the deep-water core. Profiles WC-84 and WC-89 show considerable similarities in the distribution of organic C although the concentration of organic C in

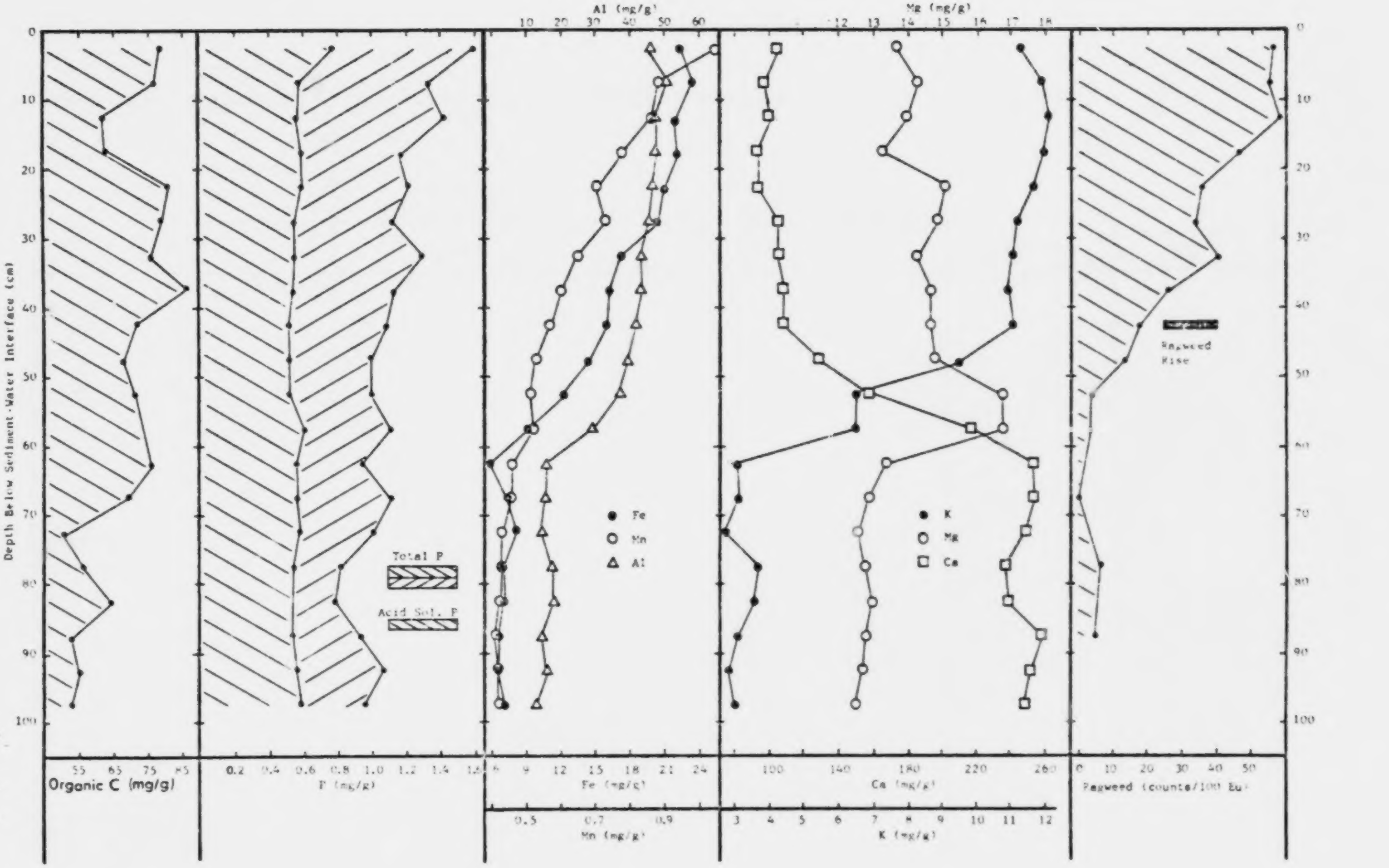


Figure 4.5 Chemical Stratigraphy of Lake Mendota Profile WC-86, University Bay.

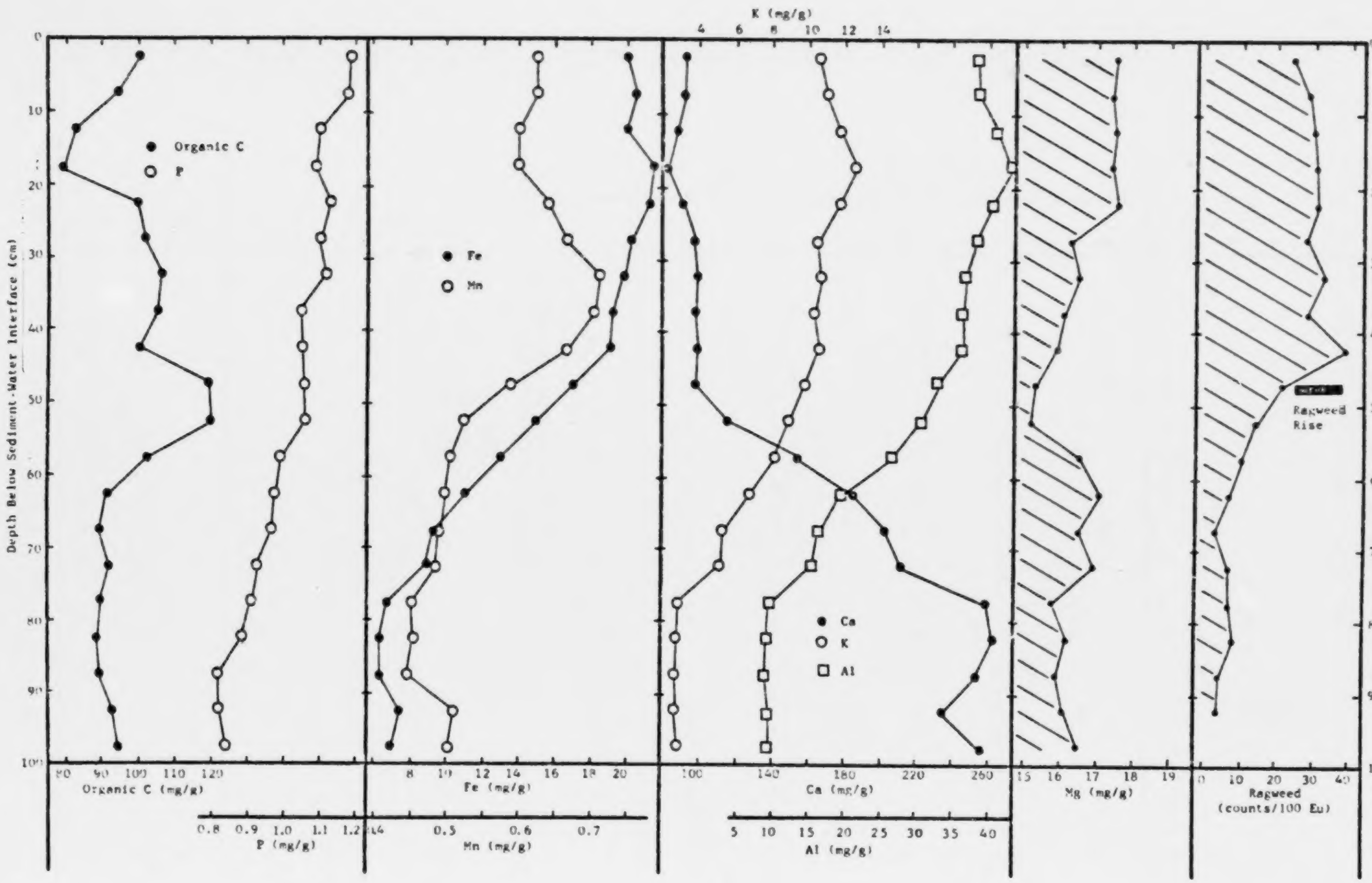


Figure 4.6 Chemical Stratigraphy of Lake Mendota Profile WC-84, University Bay.

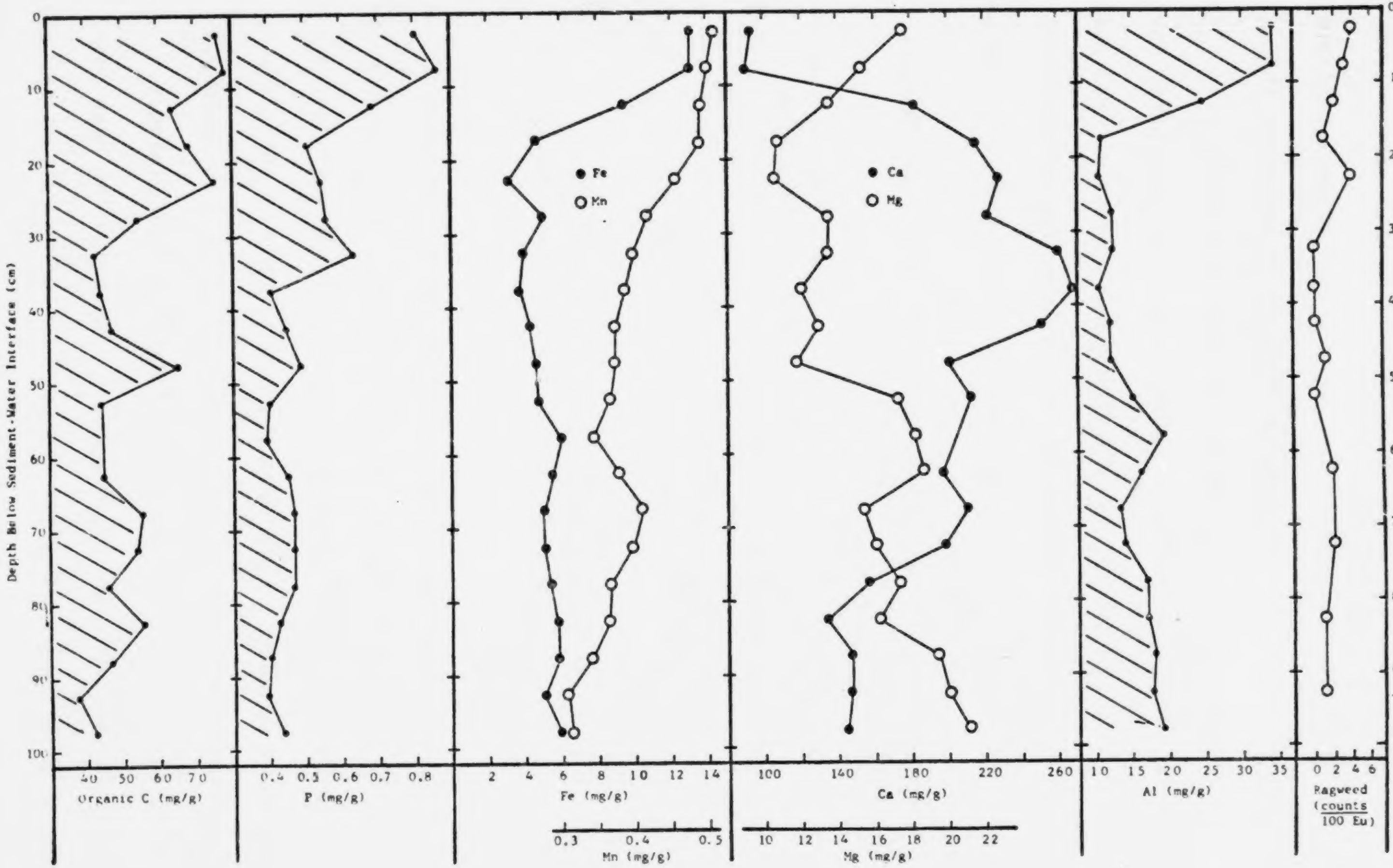


Figure 4.7 Chemical Stratigraphy of Lake Mendota Profile WC-82, University Bay.

WC-84 is higher than WC-89 throughout the core. In both profiles, WC-89 and WC-84, the mean concentration of the pre- and postcultural sediment changes only slightly; however, in cores WC-86 and WC-82 the organic C concentration is higher in the postcultural sediment.

The distribution of P increases upward in all the University Bay cores examined with the highest concentration in the postcultural sediment. The change in mean concentration of P in pre- and postcultural sediment is shown in Table 4.5 for each of the University Bay cores and the deep-water core. The mean P concentration for the precultural marl is about the same in cores WC-84, -86 and -89, but, for the same cores, the P concentration increases more in the postcultural sediment the deeper the water as shown by the mean P concentration of the postcultural sediment over the precultural sediment, P_a/P_b, in Table 4.5. The recent deposition of P in the center of the lake is probably associated with the finer sediment fraction. Although the mean concentration of P in the postcultural sediment for WC-82 follows the trend of increasing concentration with increasing water depth, the P_a/P_b ratio

Table 4.5 The Mean Concentration of Phosphorus in Pre- and Postcultural Lake Mendota Sediment.

Core	Water Depth (m)	Mean Concentration of Postcultural Sediment (P_a)	Mean Concentration of Precultural Sediment (P_b)	P_a/P_b
WC-89	23.2	1.68	0.986	1.70
WC-86	18.6	1.26	0.980	1.29
WC-84	11.2	1.12	0.924	1.22
WC-82 *	3.8	0.787	0.468	1.67

* High and low $CaCO_3$ content used to identify pre- and postcultural sediment, respectively

for the 3.8 m University Bay shallow-water core is about the same as the deep-water core. The P_a/P_b ratio is high for core WC-82 because the concentration of P in the precultural sediment is low.

In core WC-86 the acid soluble P extracted with 1 N $HCl-H_2SO_4$ is practically constant with depth of sediment, and the mean acid soluble P fraction is 47 and 58 percent of the total P in the post- and precultural sediments, respectively. In both cores, WC-86 and WC-89, a greater proportion of P is not acid extractable in the postcultural sediment. This fraction of P would probably be refractory P which is not readily exchangeable.

There is considerable parallelism in the trends for Fe, Mn, Al and K concentrations for WC-86 and WC-84. The sediments above the gyttja-marl transition zone contain about 3-4 times more Fe, Al and K and 2 times more Mn than the precultural sediment. Magnesium is nearly constant with depth for both WC-84 and WC-86, but the concentration profiles are somewhat irregular within a narrow range of 12-16 mg/g for WC-86 and 15-17.5 mg/g for WC-84.

In core WC-82, the Fe, Mn, K and Al concentrations are nearly constant for the length of the core below the 10-15 cm level, but an upward enrichment of these elements occurs above the 10-15 cm level. The Ca profile forms a peculiar shape in WC-82. Minimum concentrations of Ca are found at the bottom and top of the core, and maximum concentrations of Ca are observed at the 30-45 cm strata.

In summary, although most of the chemical components show similar trends for the cores taken in line from University Bay towards the center of the lake, there are differences in order of magnitude of the concentrations as might be expected from the surface sediment correlation data. Profile WC-82, taken in 3.8 m of water in University Bay, shows the greatest departure from the other cores in chemical stratigraphy. The individual trends for Fe, Mn, P, Mg and Ca in cores WC-84, -86 and -89 are generally alike disregarding differences in sediment depth of the postcultural sediment. Organic C reveals some similar and dissimilar trends in stratigraphy between cores WC-84, -86 and -89. The changes in order of magnitude of Fe, P and Mn concentrations with water depth of core recovery agree with the surface sample correlation data for the postcultural sediment. However, the concentrations of Fe, P and Mn are rather uniform in the precultural sediment independent of water depth, thus it appears historically the chemical composition of Lake Mendota sediments was more uniform over a greater area in the lake bottom than the recent postcultural sediments.

Long Core WC-95. The chemical stratigraphy of WC-95, a 990 cm core obtained in 24 m of water, is shown in Figure 4.8. The 9.9 m core was fractionated in 20 cm intervals and analyzed for various chemical components at 20 selected intervals. The top 62 cm of sediment consists of a black gyttja containing 22-28 percent $CaCO_3$; below 62 cm to 990 cm, the fine-grained, buff-colored marl deposits contain 46 to 57 percent $CaCO_3$. There was no variation in appearance from 62 cm to 990 cm of sediment. The depth of the postglacial marl deposits is unknown. The core is exceptionally uniform in water content with depth of sediment (see Appendix I data). Below 102 cm in the core the solids content ranges from 15.6 to 20.8 percent throughout the core, thus the original thickness of the recent sediment does not change dramatically with depth

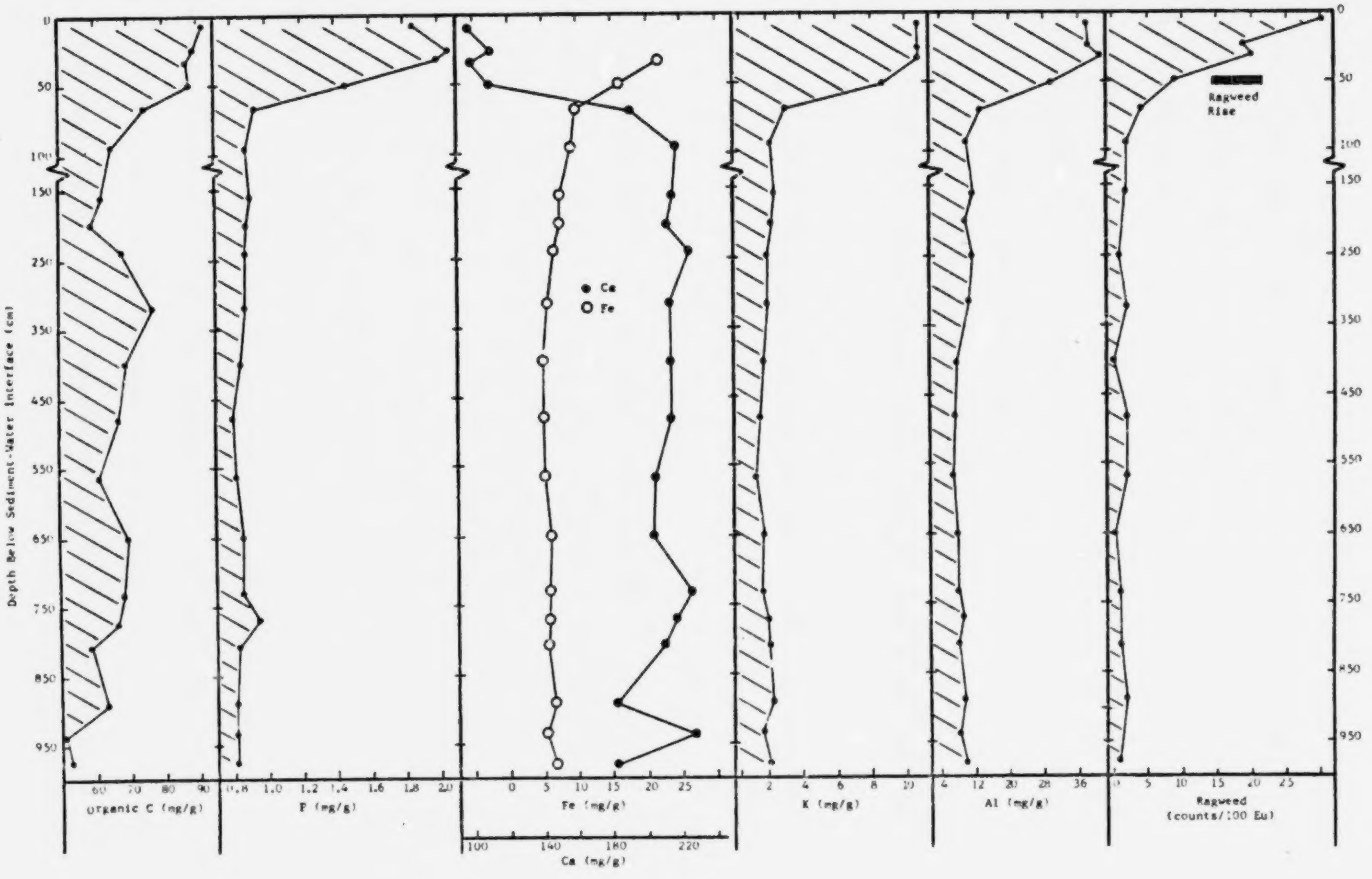


Figure 4.8 Chemical Stratigraphy of Lake Mendota Profile WC-95.

of burial because of compaction.

The marked increase in ragweed abundance occurs upward of the 42-62 cm stratum. The low ragweed pollen deposited during the period represented by 920 cm of sediment below the recent muds supports the use of Ambrosia pollen as an indicator of the cultural base in a sedimentary sequence. A ragweed maximum in pollen diagrams may not necessarily be related to European-type settlement. At Silver Lake, Ohio and at Rogers Lake, Conn., high ragweed pollen counts were found in core intervals dated 5000-8000 years B.P. (Ogden, 1966; Davis, 1967).

Organic C concentration varies from 59 to 77 mg/g over the core interval of 62-900 cm. This compares favorably with 55-73 mg organic C/g found in the marl sediment of WC-89, a short deep-water core. The postcultural sediment contains 87-92 mg/g organic C.

Phosphorus concentration remains constant at 0.8-0.94 mg/g below the ragweed horizon for a long period historically, then the P concentration increases to 1.5-2.1 mg/g in the postcultural sediment.

The depth plot of Fe, Mn, K and Al concentrations is remarkedly uniform below the ragweed horizon to 990 cm, but the postcultural concentrations of these elements increases 3-5 times that found in the precultural sediment. For all the above elemental concentrations a slight minimum inflection is observed in the zone of 400-650 cm.

In summary, the chemical stratigraphy of the 9.9 m core indicates that stable conditions existed in Lake Mendota and its watershed for a long historical period before the settlement period in Wisconsin.

Lake Monona

Deep-water Profile WC-101. The chemical stratigraphy of Lake Monona WC-101, obtained in 21 m of water, is given in Figure 4.9. The entire 1 m core is a black, homogeneous gyttja containing 22-30 percent $CaCO_3$. Sanchez (1970) found high and low concentrations of Cu above and below the 75-80 cm level, respectively. Copper sulfate was first applied to Lake Monona to control algae growth in 1918 (Nichols et al., 1946). Starting in 1925 and continuing for 29 years through 1953, copper sulfate was applied systematically to Lake Monona (Stewart and Rohlich, 1967). The depth of the Cu horizon indicates the sedimentation rate for profile WC-101 is very high. Evidence of a high sedimentation rate is also suggested by the lack of a break in the ragweed curve throughout the depth of 100 cm.

The phosphorus concentration remains nearly constant with depth and ranges from 1.3 to 1.7 mg/g. The periods of discharge of sewage effluent to Lake Monona do not seem to be reflected in the sedimentary P concentration profile. In 1936 the treatment of sewage at the Madison Burke Plant was discontinued and the discharge of sewage effluent to Lake Monona was stopped. However, in 1942 the Burke Plant was reused temporarily by the U.S. Army and by the Madison Metropolitan Sewerage District. The effluent was discharged to Lake Monona again and continued to be so discharged until 1950 (Stewart and Rohlich, 1967). Nothing is detected in the sediments that can be referred to these periodic high sources of phosphorus. However, the urban runoff to the Monona basin (Sawyer, 1944), as well as the agricultural runoff, may serve to mask any periodic high sources of phosphorus.

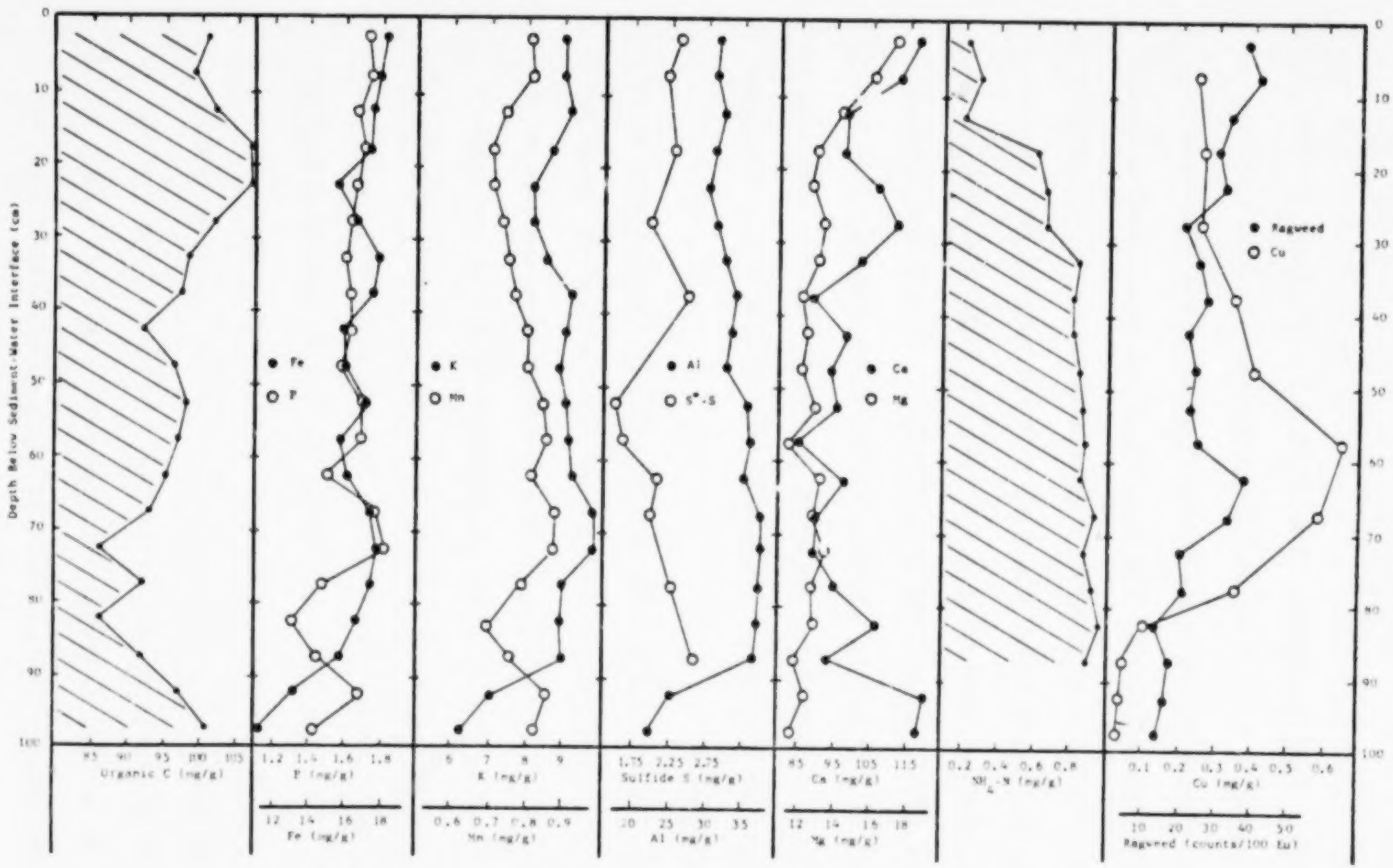


Figure 4.9 Chemical Stratigraphy of Lake Monona Profile WC-101 [Cu Data After Sanchez (1970)].

Organic C concentration decreases downward through most of the core length (15-70 cm), but there are fluctuations in the organic C profile at the top and base of the core reversing the long downward trend. Organic C decreases from 107 mg/g at 15-20 cm to 86 mg/g at 70-75 cm.

Exchangeable ammonium N decreases with depth of sediment from the surface to the 25-30 cm level and remains nearly constant with depth thereafter.

Only slight inflections with depth of sediment are observed for Ca and Mg concentrations. The only departure in the constant Mg concentration with sediment depth is the enrichment in the top 15 cm of sediment.

Mn and sulfide-S concentrations are also nearly constant with depth of sediment throughout the core. Most of the sulfide sulfur is probably held as a form of FeS. The Fe content of the recent sediment is greater than that required to hold all sulfur present as FeS; the molar ratio of sulfide sulfur to iron varies from 1:7 to 1:4.

Iron, K and Al concentrations are constant throughout the profile except a slight decrease in concentration is observed at the 90-100 cm level.

In general, the chemical composition of the deep-water core WC-101 is strikingly uniform with depth of sediment.

Profile WC-46. The chemical stratigraphy of Monona core WC-46, obtained in 15.9 m of water, is given in Figure 4.10. The top 35 m of sediment is a black gyttja, followed by a 20 cm transition zone to a buff-colored marl, which is dominant from 60-95 cm. The gyttja and marl layers contain 27-30 percent and 47-60 percent $CaCO_3$, respectively.

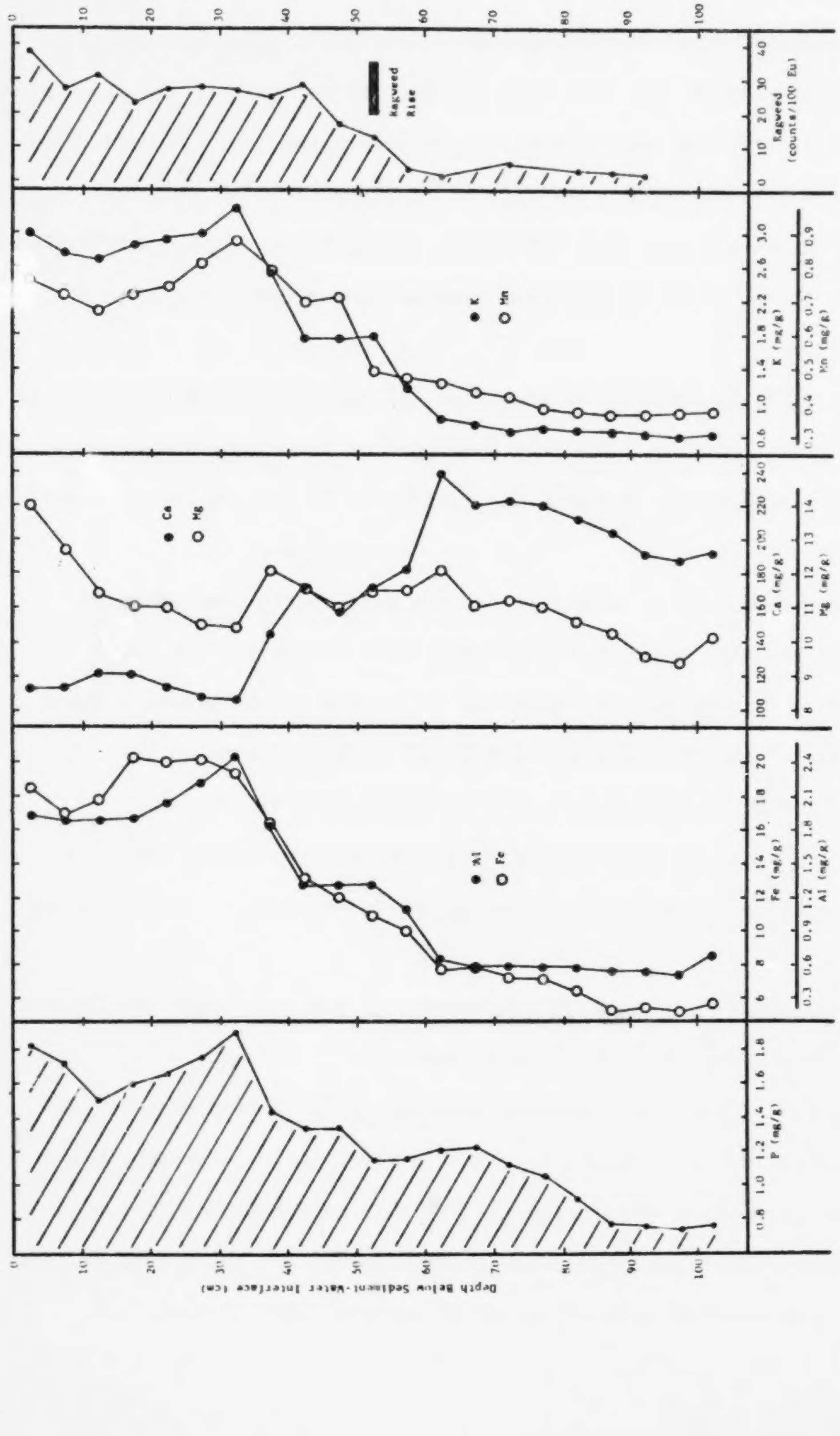


Figure 4.10 Chemical Stratigraphy of Lake Monona Profile WC-46.

Ragweed pollen increases upward at the 50-55 cm horizon which coincides with the transition zone from high to low Ca content.

The P concentration of 0.7-1.9 mg/g generally increases upward from the 80-85 cm level to the surface sediment; below 80 cm, P concentration remains constant. The initial increase in P concentration at the 80-85 cm interval, 30 cm below the ragweed horizon, is followed by another rise in P concentration at the 45-50 cm interval corresponding closely to the ragweed horizon. The P concentration increases to a maximum peak at the 30-35 cm interval (ca. 50 years B.P.) and remains high thereafter to the sediment surface.

Iron and Mn concentration profiles are very similar to the P distribution pattern. Below 60 cm, iron and Mn increase from a background concentration of 5.2-7.8 mg/g and 0.37-0.46 mg/g, respectively, to 2-3 times these concentrations in the postcultural sediments.

Above 60 cm coinciding with the initial rise in ragweed (50-55 cm), the Al and K increase rapidly to maximum concentrations at the 30-35 cm interval and remain high thereafter to the sediment surface. From a low background concentration in the precultural sediment, Al and K concentrations increase 3-4 times and 4-5 times in the postcultural sediment, respectively.

Calcium concentration increases upward from 190 to 240 mg/g over the interval 105-60 cm. From 60 cm to the surface sediment the Ca profile forms a mirror image to the K, Al, P, Fe and Mn concentration profiles.

On the other hand, Mg concentration changes only slightly with depth but increases in the top 15 cm of sediment.

The results indicate that P, Fe, Mn and Ca concentrations of cores WC-101 and WC-46 are the same order of magnitude upward of 35 cm in each core sequence. The apparent uniformity in the elemental concentration with water depth is in agreement with Twenhofel's observation (1937). He collected core samples from Lake Monona along a transect from Turville Point to Southwest of the Yahara River and found from a profile of the traverse that the percentages of $CaCO_3$, insoluble residue and loss on ignition were regular and uniform over the main part of the traverse, but fluctuated greatly in the shallow water.

Lake Wingra

The chemical stratigraphy of Lake Wingra core WC-92 is shown in Figure 4.11. The top 60 cm consists of a gray marl deposit of 56-62 percent $CaCO_3$; below 60 cm the gray marl is 68-80 percent $CaCO_3$ and contains many gastropod shells and shell fragments. The sediments appear coarse because of the shell fragments, but the matrix between the shells is fine-grained. Juday (1914) noted the large marl deposits both on the bottom of Lake Wingra and along its margins. In some places these deposits reached a thickness of 8 to 9 m according to Juday (1914).

The marked increase in ragweed abundance occurs upward of the 65-70 cm horizon. The depth of the ragweed horizon indicates the sedimentation rate for Lake Wingra is high.

The organic C and organic N concentration profiles are closely related. Even though the organic C is somewhat irregular, each irregularity is duplicated by the organic N depth plot. A minimum concentration

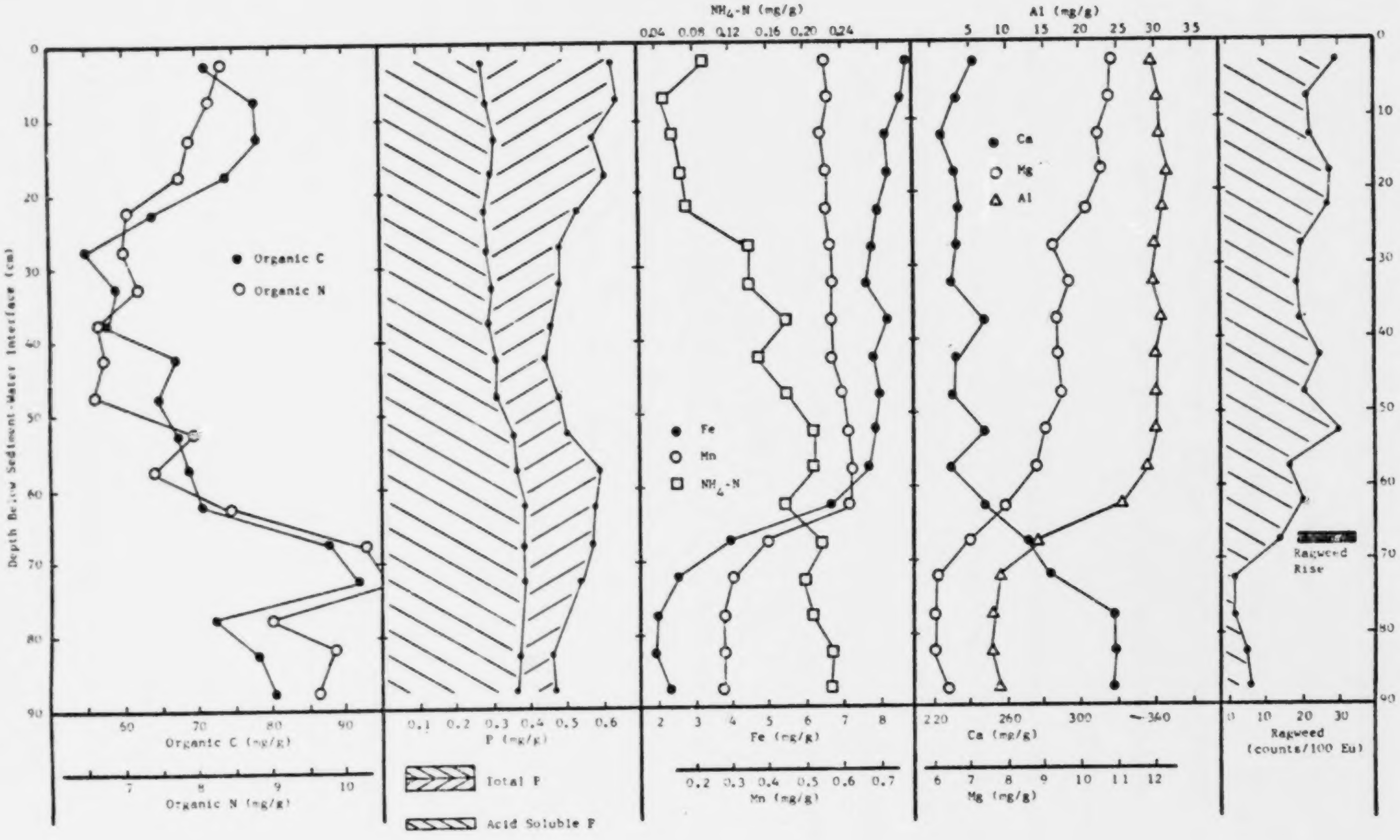


Figure 4.11 Chemical Stratigraphy of Lake Wingra Profile WC-92.

of 55-70 mg/g organic C is found from 55 to 25 cm in the postcultural sediment, and a maximum concentration of 72-92 mg/g organic C is found from 90 to 65 cm in the precultural sediment. There is a rise in organic C and organic N in the top 20 cm of sediment which is estimated to contain material deposited 20-30 years ago based on the ragweed rise at 100 years B.P.

Exchangeable ammonium N concentration increases with depth of burial throughout the postcultural sedimentary sequence; in the precultural sediment the exchangeable ammonium N concentration remains nearly constant at 0.20-0.23 mg/g which is approximately four times greater than the lowest concentration found in the uppermost 25 cm of sediment.

Total P concentration fluctuates slightly with depth of sediment ranging from 0.45 to 0.64 mg/g. Minimum P concentration (0.45-0.51 mg/g) corresponds to the minimum organic C and organic N concentration at the 55-25 cm interval. Upward of 25 cm (ca. 35-40 years B.P.) phosphorus concentration increases slightly. Acid soluble P extracted with 1 N $HCl-H_2SO_4$ varies from 0.27 to 0.39 mg/g throughout the core. The highest concentration of acid soluble P is found in the precultural sediment which contains the larger fraction of $CaCO_3$ and organic C and the smaller fraction of Fe, Al, Mn and Mg. The proportion of acid soluble P to total P varies from 43-69 percent to 66-81 percent in the postcultural and precultural sediment, respectively. In other words, the postcultural sediment contains a greater proportion of P which is not acid extractable. Presumably, the more recent muds contain more P which is refractory or not readily exchangeable to the overlying water.

As a first approximation, the fraction of P released with 1 N acid includes inorganic P (Ca-P plus Al-P and Fe-P), but 1 N acid probably would not extract organic P or occluded forms of Fe-P and Al-P (Shah et al., 1968).

The chemical stratigraphy of profile WC-92 changes considerably at the 65-70 cm boundary horizon. The precultural deposits below the 65-70 cm stratum contain low concentrations of Fe, Mn, Al, K and Mg. These elemental concentrations increase sharply upward from 65-70 cm into the postcultural sediment and level off above 55 cm to the surface sediment. Iron, Mn and Al concentrations increase 3-4 times in the postcultural sediment compared to the precultural sediment.

Comparison of Pre- and Postcultural Sediments in Calcareous Lakes

The mean concentration of various chemical components of the pre- and postcultural sediments of Mendota, Wingra and Monona are given in Table 4.5. A comparison of the mean concentration of postcultural over precultural sediment is presented as a ratio, K, in Table 4.6. If K is plus or minus 10 percent of unity, the notation of zero is given for little or no decrease or increase in the mean postcultural over precultural concentration. Likewise, arbitrary notation is given for K denoting increases or decreases of 20 and 50 percent in postcultural over precultural sedimentary concentrations.

There is considerable uniformity in the individual distribution patterns of P, Fe, Mn, Al, K, Mg and Ca between the Lake Mendota cores. The postcultural sediments are enriched in P, Fe, Mn, Al and K compared to the precultural sediment which is enriched in Ca only. Magnesium concentration remains about the same throughout the core. Organic C is

Table 4.6 Mean Concentrations of Pre- and Postcultural Sedimentary Components for Calcareous Lakes.

Core		Org-C	P	Fe	Al	K	Mg	Ca	Mn
		mg/g							
Lake Mendota									
* WC-89	a	73.5	1.68	21.2	--	10.1	11.1	112	1.16
	b	71.4	0.986	10.9	--	5.40	10.3	159	0.485
WC-86	a	74.3	1.26	20.1	45.9	11.5	14.3	102	0.762
	b	61.1	0.976	8.29	21.1	4.32	13.7	228	0.460
WC-84	a	98.7	1.11	19.9	38.3	11.0	16.8	94.0	0.644
	b	94.6	0.919	9.07	15.7	4.77	16.3	214	0.486
** WC-82	a	73.4	0.787	11.9	30.8	9.18	15.5	122	0.500
	b	51.9	0.468	5.03	14.6	4.82	15.6	199	0.382
WC-95	a	89.1	1.85	19.2	37.1	10.3	--	102	1.04
	b	64.8	0.854	6.59	9.45	2.01	--	210	0.364
Lake Monona									
WC-101	a	97.1	1.63	16.5	32.5	8.81	13.2	101	0.790
	b	--	--	--	--	--	--	--	--
* WC-46	a	--	1.57	16.8	1.83	2.58	11.4	131	0.723
	b	--	0.976	6.83	0.63	0.73	10.6	207	0.400
Lake Wingra									
WC-92	a	68.9	0.545	7.72	29.0	5.06	9.53	238	0.571
	b	80.7	0.490	2.17	8.57	0.66	6.14	310	0.288

a Mean concentration of postcultural sediment

b Mean concentration of precultural sediment

* $HClO_4$-HNO_3 digestion (w/o HF), except K determination for Lake Mendota core WC-89

** High and low $CaCO_3$ content used to identify pre- and postcultural sediment the only chemical component which deviates from the consistent pattern in the horizontal stratification of the deep-water and University Bay cores. The K values for organic C in cores WC-89 and WC-84 are zero, whereas the other three Lake Mendota cores exhibit an increase in organic C concentration in the postcultural sediment. In general, the deposition is rather uniform horizontally between the deep-water and University Bay cores. The ragweed pollen data suggest different rates of deposition in each of the Lake Mendota cores.

The mean Ca concentration increases in the Lake Mendota postcultural sediment with increasing water depth from core WC-84 to WC-89. This observation is in agreement with a comparison of the geographic distribution of $CaCO_3$ content of the gyttja and marl made by Murray (1956). He found that the gyttja contained higher concentrations of $CaCO_3$ and the marl contained lower concentrations of $CaCO_3$ as the depth of the water increased. Furthermore, this study indicates Mg concentration decreases with increasing water depth for both the pre- and postcultural sediments. Thus, it appears that prior to the deposition of black gyttja sedimentary Ca and Mg concentration behaved similarly with respect to water depth but in the postcultural sediment Ca and Mg concentrations are inversely related with respect to water depth of core recovery.

The postcultural sediment of Monona core WC-46 is enriched in P, Fe, Mn, K and Al compared to the precultural sediment which is enriched in Ca only. Magnesium concentration remains relatively constant throughout the core. Similar trends are observed for Mendota.

The positive K values (see Table 4.7) for the chemical stratigraphy

Table 4.7 Comparison of Mean Concentration of Postcultural over Precultural Sedimentary Components in Calcareous Lakes.

Core	Org-C	P	Fe	Al	K	Mg	Ca	Mn
	$\underline{K}$*							
Mendota								
WC-89	0	+++	+++	n.d.	+++	0	--	+++
WC-86	++	++	+++	+++	+++	0	---	+++
WC-84	0	++	+++	+++	+++	0	---	++
WC-82	++	+++	+++	+++	+++	0	--	++
WC-95	++	+++	+++	+++	+++	n.d.	---	+++
Monona								
WC-46	n.d.	+++	+++	+++	+++	0	--	+++
Wingra								
WC-92	-	0	+++	+++	+++	+++	--	+++

$$* \ \underline{K} = \frac{\text{mean concentration of postcultural sediment}}{\text{mean concentration of precultural sediment}}$$ (see Table 4.6)

Notation: $1.1 \geqslant \underline{K} \geqslant 0.9$ = 0

$1.1 < \underline{K} \leqslant 1.2$ = +

$0.9 > \underline{K} \geqslant 0.8$ = -

$1.2 < \underline{K} \leqslant 1.5$ = ++

$0.8 > \underline{K} \geqslant 0.5$ = --

$\underline{K} > 1.5$ = +++

$\underline{K} < 0.5$ = ---

n.d. = no determination

of Wingra are similar to Mendota and Monona except for organic C, P and Mg. In the Wingra sediments organic C increases in the precultural sediment, while P remains constant with sediment depth and Mg increases in the postcultural over the precultural sediment.

The order of magnitude of the various chemical components in the postcultural sediment is very similar for Mendota and Monona. The lower concentrations of P, Fe, Mn, Mg and Al in Wingra sediments may be partially attributed to the high carbonate-containing sediment diluting the above fractions. Nevertheless, organic C concentrations in the post- and precultural sediment of Wingra are the same order of magnitude as found for Mendota and Monona.

C. Chemical Stratigraphy of Noncalcareous Northern Wisconsin Lakes and Devils Lake in Southern Wisconsin

Cores were taken from two deep-water locations in Little St. Germain, Minocqua and Trout lakes. The shoreline of these lakes is irregular, and the lakes are separated into two or more bay areas. Single cores were taken from the deep-water locations of the lakes with more or less symmetrical basins--Devils, Little John, Weber and Sparkling lakes.

Little St. Germain

West Bay Profile WC-92. The chemical stratigraphy of Little St. Germain core WC-92, obtained in the deep-water of the West Bay is given in Figure 4.12. The sediment consists of a brown-black gyttja throughout the 85 cm core. The abrupt rise in ragweed pollen at the 35-40 cm level separates the pre- and postcultural sediment. The most striking feature of the core is the change in chemical stratigraphy corresponding to the initial rise in ragweed pollen.

Organic C concentration increases with depth of sediment. The greatest change in organic C determination occurs at the 35-40 cm ragweed boundary horizon. Below 35-40 cm in the precultural sediment organic C concentration is 186-240 mg/g, and above 35-40 cm in the postcultural sediment organic C decreases to 122-182 mg/g. The organic C profile is closely related to Fe, Mn and P distribution.

Phosphorus concentration decreases in the postcultural sediments by approximately one-half that of the precultural sediment. A minimum concentration of P (7.4-10.5 mg/g) occurs at the 15-35 cm strata which probably represents sediment deposited approximately 40-100 years ago. The sediments laid down at this time were probably associated with the maximum

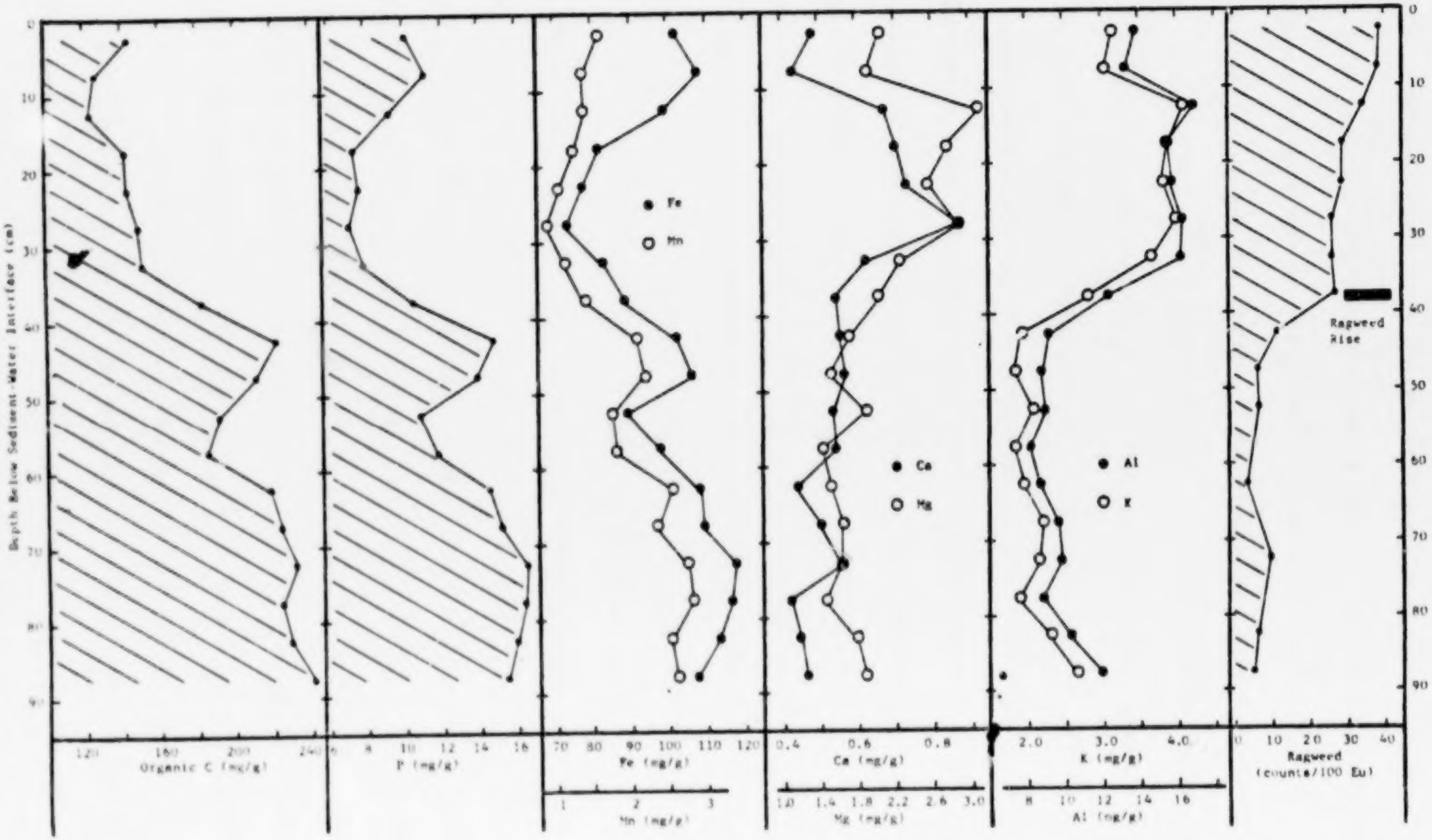


Figure 4.12 Chemical Stratigraphy of Little St. Germain Profile WC-92, West Bay.

disturbance in the watershed from deforestation in northern Wisconsin.

Phosphorus, Fe and Mn concentration profiles are closely related. The close association is especially illustrated in the small minimum peak followed separately by P, Fe and Mn at the 50-60 cm level. Presumably, the depositional efficiency of P is influenced by the Fe-Mn cycle. Of particular interest in connection with the P, Fe and Mn distribution is Mackereth's (1966) interpretation of the postglacial sedimentation of these elements in English lakes. Mackereth felt the two major processes involved in the sedimentation of P were coprecipitation of P with oxidized Fe and Mn compounds and precipitation of P incorporated in the organic material synthesized in the lake. In the sediment of Ennerdale, an unproductive lake, the profiles of Fe and P concentrations were inversely related as the sediment surface was approached; Fe rose steadily in concentration, while P decreased. Mackereth explained that the precipitation efficiency for P in Ennerdale basin has not been influenced by variations in the Fe-Mn cycle, but the precipitation of P was largely biological and relatively constant. On the other hand, Mackereth believed that the P concentration was directly related to Fe and Mn distribution in the sediment of Esthwaite, a productive lake, and that the P minimum in the core profile resulted directly from loss of Fe and Mn from the lake. Since the P, Fe and Mn profiles are so closely related, it must be presumed that a very important part is played by both Fe and Mn, not only in the deposition of P to the sediment but also its retention therein.

Calcium and Mg concentration profiles form a mirror image to P, Fe and Mn distribution patterns, and maximum Ca and Mg concentrations occur at the 10-30 cm strata in the postcultural sediment.

Aluminum and K concentrations show a distribution pattern similar to Ca and Mg. The greatest increase in Al and K coincides with the initial rise in ragweed pollen at the 35-40 cm horizon. The maximum concentrations of Al, K and Mg are probably associated with increased deposition of eroded clay minerals.

Upward in the top 10 cm of sediment, P, Fe and Mn concentrations increase and Ca, Mg, Al and K concentrations decrease. This recent trend in the last 30-40 years may indicate a change toward the sediment conditions of the precultural period.

South Bay Profile WC-56. The chemical stratigraphy of Little St. Germain core WC-56, obtained in 7 m of water from the South Bay is given in Figure 4.13. The greenish-black deposits contain macroscopic fragments of undecomposed vegetation. The top three sections were combined as a composite sample because of insufficient dry material in each 5 cm section.

The depth of the ragweed boundary is somewhat questionable. There appears to be a secondary rise in ragweed at the 65-70 cm interval which closely corresponds to the major change in chemical stratigraphy. If the secondary rise in ragweed is accepted as the actual point in the core sequence where the major cultural influence took place, the cores from West Bay and South Bay would be congruous. If the increase at the 40-45 cm interval is considered the ragweed boundary rise, then it appears that considerable changes in concentration of P, Fe, Mn and organic C occurred prior to the major cultural influence of approximately 100 years B.P. There are three possible reasons for accepting the rise at 65-70 cm as a marker of the cultural influence. The small number of ragweed counts between 70-40

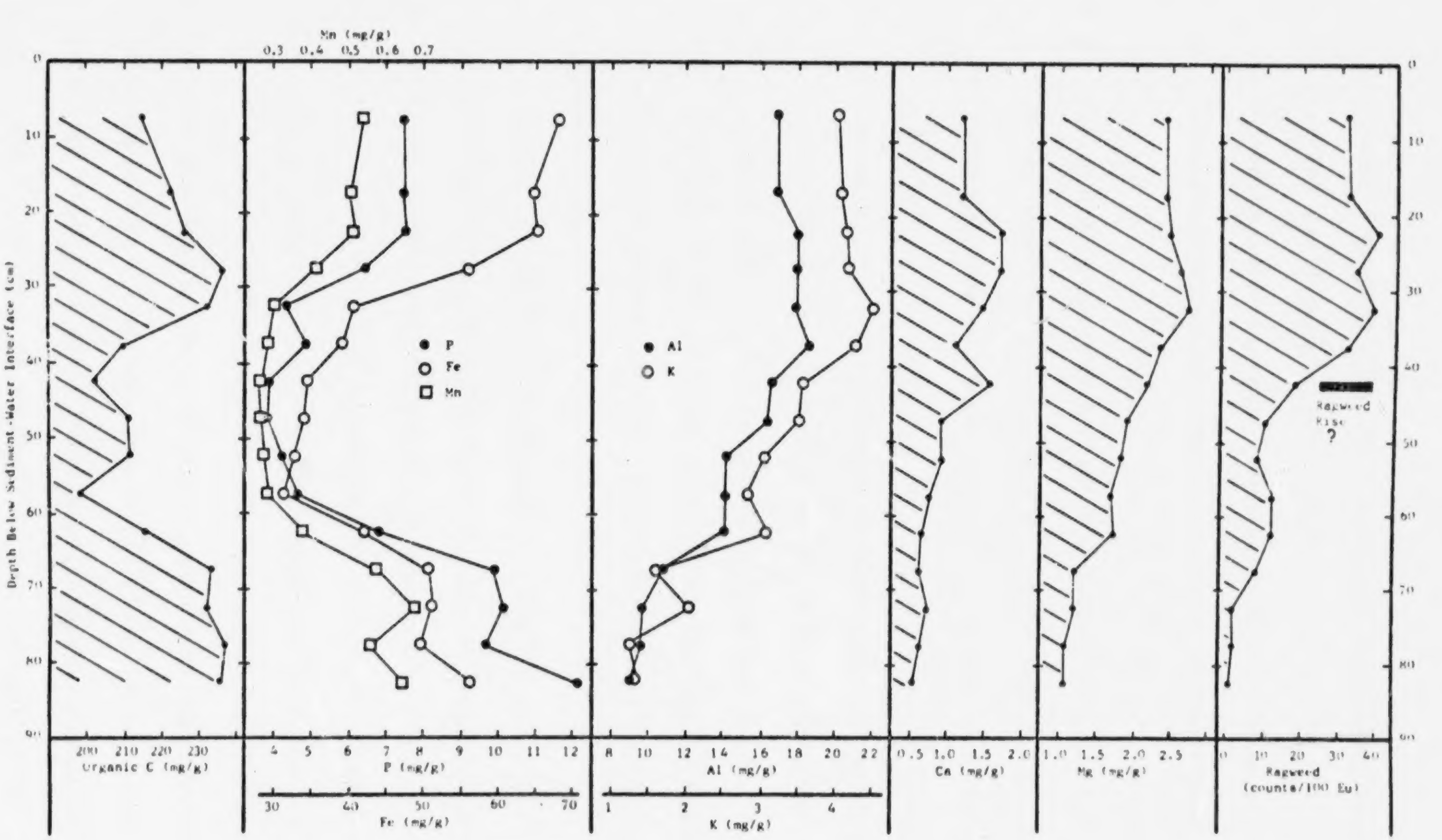


Figure 4.13 Chemical Stratigraphy of Little St. Germain Profile WC-56, South Bay.

cm may have resulted from the dilution of pollen in the sediment matrix by an increased sedimentation rate of mineral components. Second, the ragweed pollen accumulated in the sediment may not have been as responsive as the chemical changes manifested in the core sequence. Thus, a lag in the pollen diagram compared to the chemical stratigraphy is observed. Third, the sedimentation rate of South Bay could conceivably be higher than West Bay because South Bay is a shallow bay with an extensive littoral area which is highly productive in aquatic weed growth. South Bay is also in line with the inlet-outlet system, whereas in West Bay the incoming material is from direct surface runoff, groundwater and rainfall. With some reservation, the secondary rise in ragweed at 65-70 cm will be taken as the cultural base in the South Bay of Little St. Germain.

Phosphorus, Fe and Mn distribution patterns are again similar to each other; however, the concentrations are lower in South Bay than West Bay. The importance of obtaining a core of sufficient length to include the background precultural sediment is shown in profile WC-56. For example, if the core were only 60 cm long, the interpretation might be that P, Fe and Mn concentrations in the top 30 cm are enriched due to the cultural influences. However, below 60 cm, P, Fe and Mn increase markedly with depth of sediment to the 65-70 cm level. Thus, the impression would be that the main cultural effect is represented by the 60-30 cm interval in the core sequence and the top 30 cm of sediment deposited in the last 35-40 years shows the P, Fe and Mn concentration shifting back towards the levels found in the precultural sediment.

Aluminum and K concentration remain constant in the top 35 cm of postcultural sediment, but in the postcultural sediment (70-35 cm) an upward increase in Al and K is observed. The Ca and Mg profiles show trends similar to Al and K.

Long Core L-73. The chemical stratigraphy of Little St. Germain core L-73, obtained in 3.1 m of water near the outlet of the South Bay, is given in Figure 4.14. The 724 cm core obtained by Charlton (1969) penetrated the depth of the postglacial deposits; the generalized sequence of sediment is a homogeneous organic mud, or gyttja, above clear quartz sand. The organic mud recovered in the cores did not show any variation in appearance with depth (Charlton, 1969). Ragweed pollen was not found throughout the core sequence. This is probably best attributed to the shallow-water recovery of the core. Apparently, ragweed pollen does not settle to the bottom muds in regions of the lake where the water is mixed to keep the pollen resuspended. The C-14 dates shown on Figure 4.14 were obtained by Charlton (1969).

The change in organic C is quite pronounced during the early history of Little St. Germain. Organic C increases from 215 mg/g at the base of the core to 330 mg/g at the 400 cm level. Based on the C-14 date, this increase occurred over a period of at least 6500 years. Above 400 cm to the sediment-water interface, the change in organic C concentration stabilizes and fluctuates only slightly from 333 mg/g to 391 mg/g. However, in the most recent muds, upward of 38 cm, organic C concentration remains high at 382-391 mg/g. A similar postglacial distribution pattern for organic C has been observed in Windermere and Ennerdale Water in England by Mackereth (1966) and in Linsley Pond by Hutchinson and Wollack (1940). The distribution of organic matter in Linsley Pond profile was believed by Hutchinson and Wollack (1940) to indicate a rapid change from oligotrophy

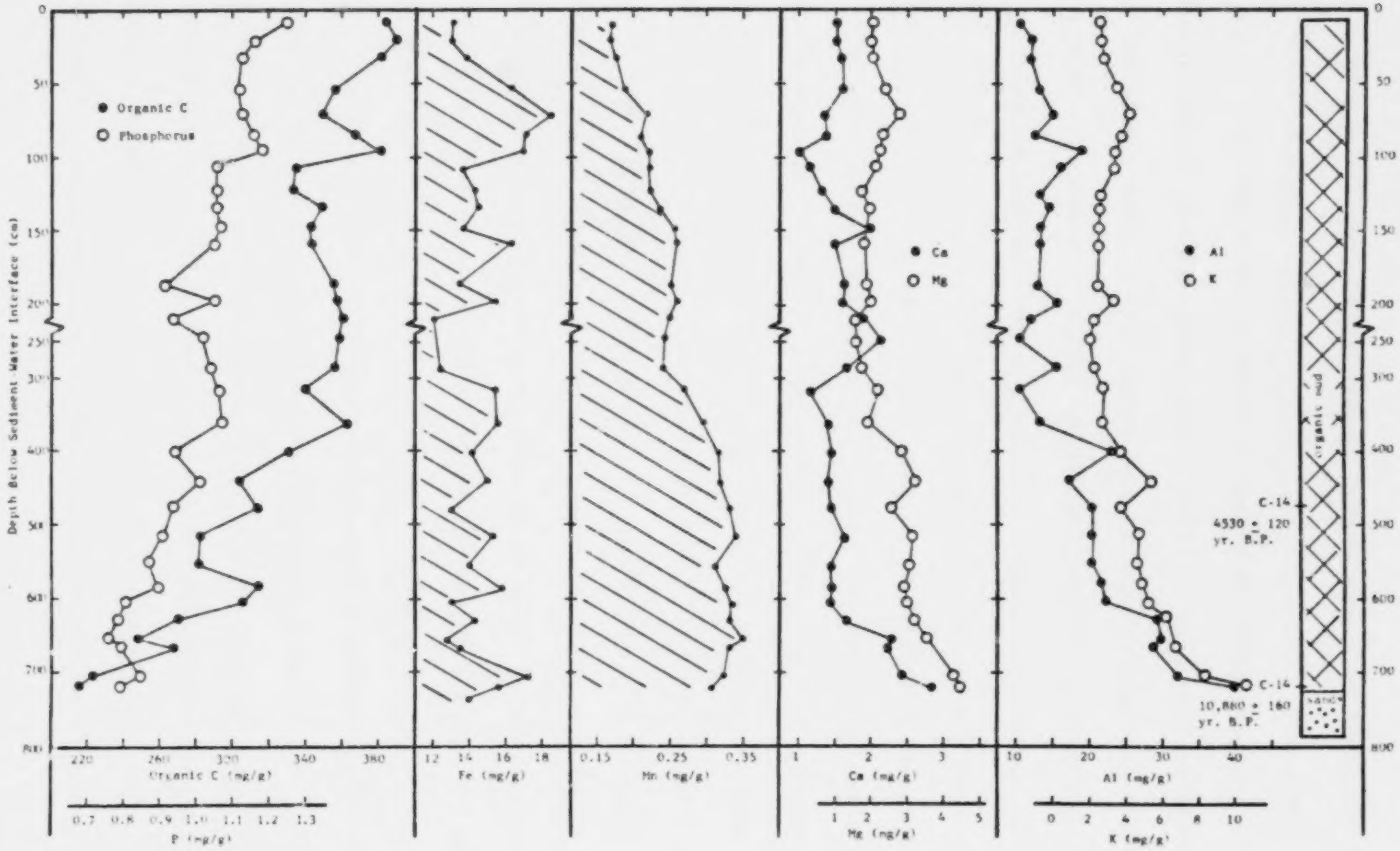


Figure 4.14 Chemical Stratigraphy of Little St. Germain Profile L-73, South Bay [Carbon-14 Data After Charlton (1969)] .

to eutrophy followed by a long period of approximate equilibrium in eutrophic conditions.

Maximum concentrations of organic C occur in the upper half of the mud column for profile L-73. Gorham (1961) noted maximum concentrations of chlorophyll derivatives, sulfur and carbon were reached slowly in Ennerdale, an unproductive lake, but in Esthwaite, a productive lake, all three constituents showed a rapid rise deep in the mud column, which implies the lake became eutrophic early in its history.

Phosphorus distribution is parallel to organic C concentration throughout the core sequence. The association of P, Fe and Mn with organic C is characteristic of the Little St. Germain cores. However, throughout the long core sequence of L-73 the distribution pattern of Fe and Mn is not associated with P and organic C. Neither is there a close association of P, Fe and Mn profiles to each other. Iron fluctuates with depth from 12-18.6 mg/g with no discernible increasing or decreasing trend. On the other hand, Mn steadily increases with depth of sediment throughout late postglacial period from the sediment-water interface to the 400 cm level; phosphorus, organic C and Fe remain more or less constant throughout this period. Below the 400 cm horizon Mn remains constant with depth of sediment.

Calcium, Mg, Al and K concentrations increase upward from the base of the core to approximately 400 cm. Above the 400 cm level these elemental concentrations remain constant or fluctuate only slightly to the sediment-water interface. The basal enrichment of Al, Mg and K probably indicates the sediment was rich in eroded clays and silts in early postglacial time.

Trout Lake

South Bay Profile WC-59. The chemical stratigraphy of Trout Lake core

WC-59, obtained in the deep-water area of the South Bay is given in Figure 4.15. The sediment consists of a dark-greenish-gray to black gyttja. The organic mud recovered in the cores did not show any variation in appearance with depth of sediment. The ragweed pollen increases sharply upward at the 35-40 cm level separating the pre- and postcultural sediment. However, it is noteworthy that there are shifts in the chemical composition of the 105 cm core sequence above and below the ragweed horizon boundary.

The profile of organic C concentration correlates almost exactly with organic N. Even though the organic C profile is fluctuating, the overall trend is an increase in organic C with depth of sediment. The minimum organic C (135-187 mg/g) in the postcultural sediment is probably associated with the maximum disturbance from deforestation in the watershed; however, a minimum organic C peak also occurs at the 45-65 level in the precultural sediment.

Exchangeable ammonium N increases with depth of burial. The general increase in exchangeable ammonium N with depth may indicate that organic materials are undergoing decomposition to ammonia. The ammonium N accumulated may therefore be that formed in situ. Although the exchangeable ammonium concentration increases in the deeper layers, it makes up only a small fraction of the organic nitrogen present.

Phosphorus, Fe and Mn concentration profiles are closely related throughout the core sequence. The highest concentration of P (6.7-7.8 mg/g) is found in the top 10 cm of sediment. Phosphorus and Mn concentrations fall within a range of 4-6 mg/g and 2-3.5 mg/g, respectively, except for departures at three intervals--minimum peaks at 90-95 cm and 35-40 cm and a maximum peak at 0-10 cm. However, Fe concentration remains constant

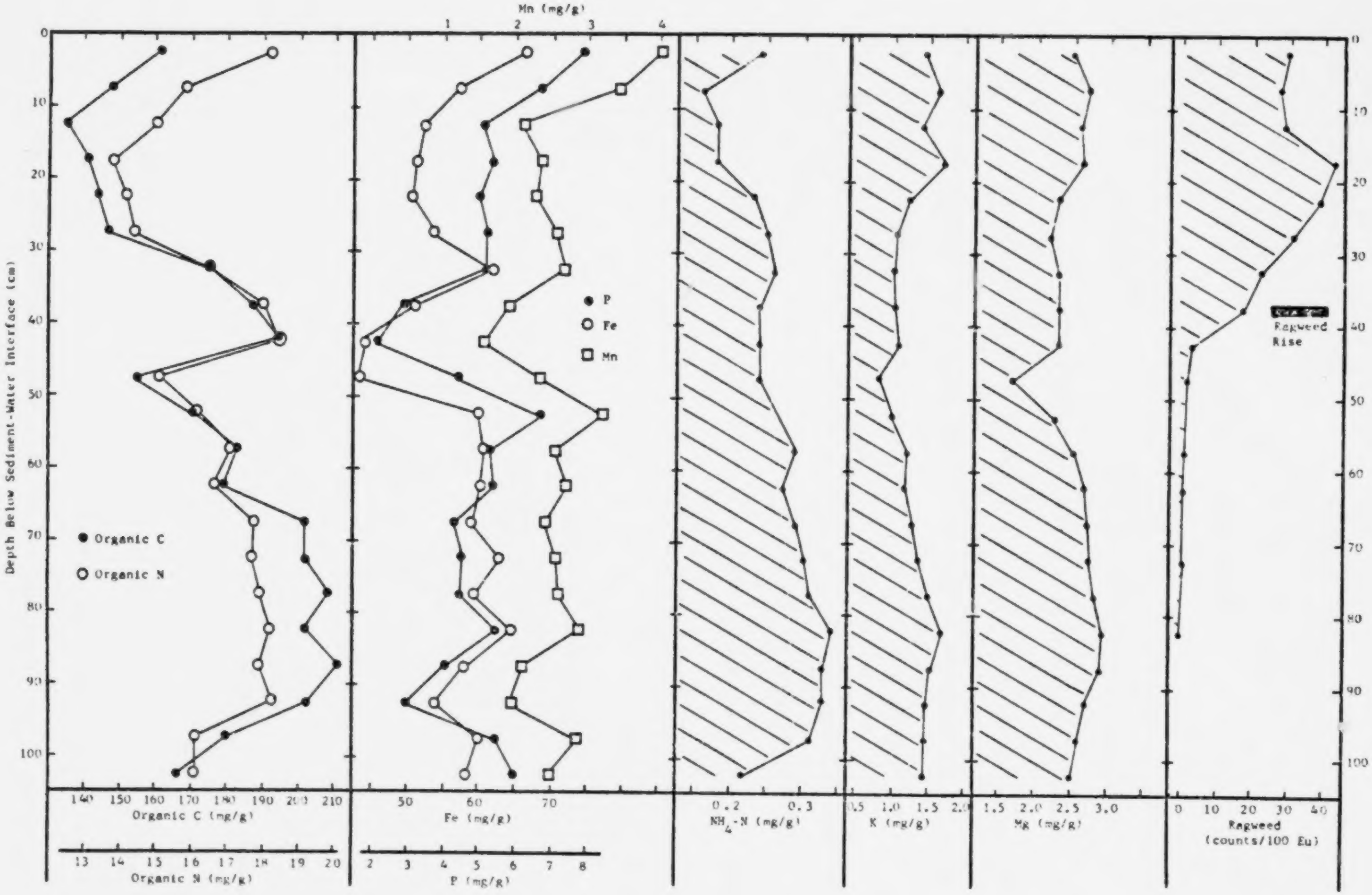


Figure 4.15 Chemical Stratigraphy of Trout Lake Profile WC-59, South Bay.

below 50 cm in the precultural sediment and fluctuates considerably above 50 cm.

Potassium and Mg concentration change only slightly with depth of sediment. In contrast to the Little St. Germain cores, K and Mg concentrations do not increase in the postcultural sediment to form a mirror image to organic C, which might be expected if sedimentation of eroded clastic material increased concurrently to deforestation.

The oscillations in the chemical stratigraphy of South Trout, which apparently do not necessarily correlate with the ragweed horizon, may be due to a phenomenon peculiar to Trout Lake. Bottom convection currents along the steep bottom banks of South Trout may cause the sediments to slump. Thus, sediment which is eroded from the steep slope and redeposited to the basin floor may account for the observed fluctuations in the sedimentary profile. Gould and Budinger (1958) point to convection currents as being agents responsible for the observed inequalities in limnic-peat sedimentation in Lake Washington which occupies a deep narrow trough. Apparently, in Lake Washington convection currents associated with winter overturn have extended to the deepest part of the lake to erode and redeposit sediments.

North Bay Profile WC-60. The chemical stratigraphy of Trout Lake core WC-60, obtained in the center of the North Bay in the deep-water area, is given in Figure 4.16. The sediment consists of a dark-greenish gray to black gyttja much the same as South Trout. The ragweed pollen increases upward fairly abruptly at the 25-30 cm horizon. Contrary to South Trout, some of the major changes in chemical stratigraphy of North Trout coincide with changes in the ragweed profile. Based on the ragweed pollen profile,

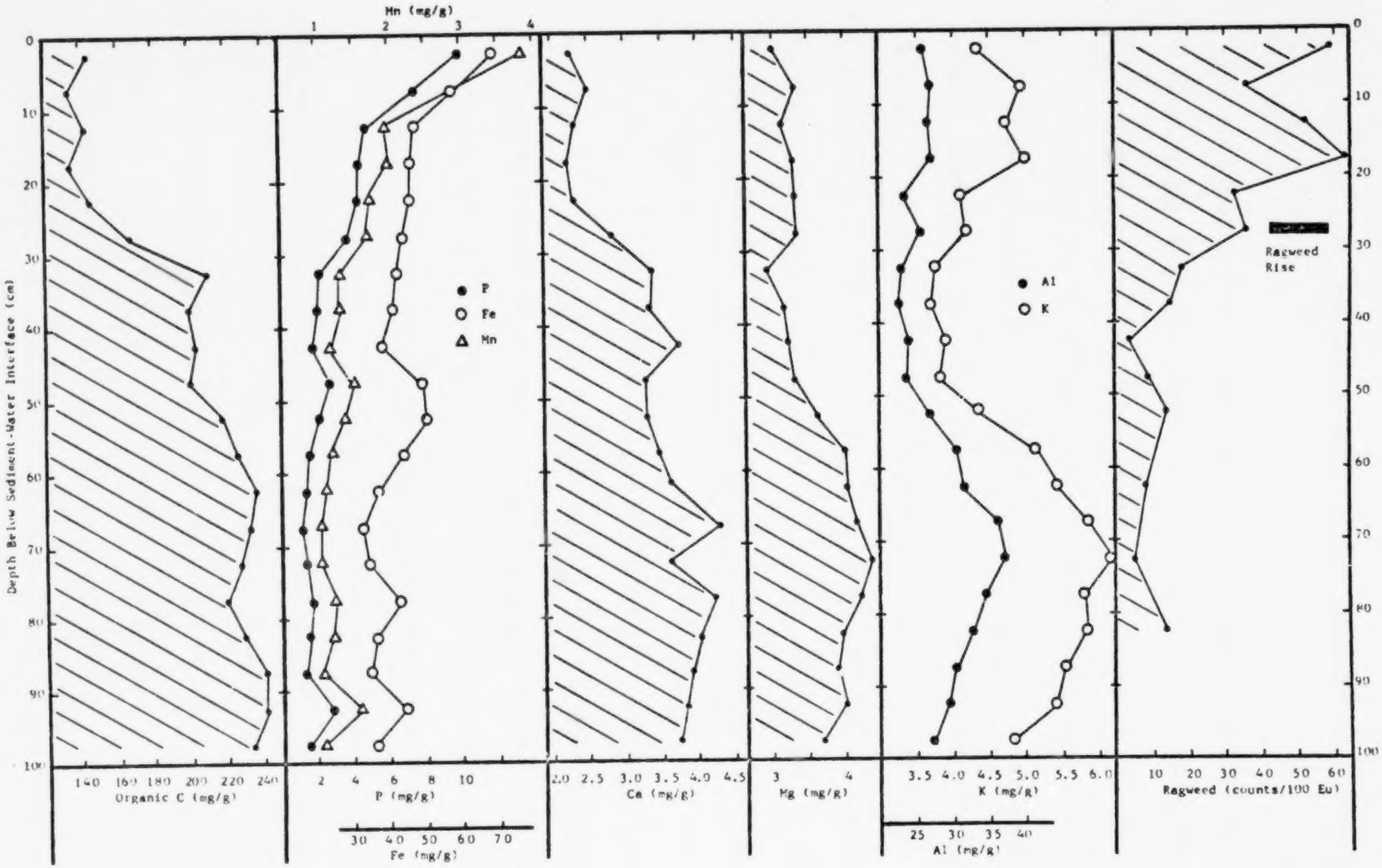


Figure 4.16 Chemical Stratigraphy of Trout Lake Profile WC-60, North Bay.

the sedimentation rate of North Trout is less than South Trout.

Organic C concentration (134-167 mg/g) is lowest in the postcultural sediment. The largest upward decrease in organic C occurs simultaneously with the break in the ragweed curve. Even though organic C concentration generally increases with depth, it appears that organic C deposition is represented by the following three trends: (1) constant concentration (95-65 cm), (2) an upward decrease (60-30 cm) and (3) an accelerated upward decrease in the postcultural sediment.

Phosphorus, Fe and Mn distribution patterns again show a strong association to each other and form a mirror image to organic C. For both South and North Trout cores, P, Fe and Mn become enriched in the uppermost 10 cm. The concentration of P in the top 10 cm is 7.4-9.9 mg/g which is approximately 4-5 times higher than the mean concentration of P found in the precultural sediment. The top 10 cm of sediment is probably represented by sediments deposited 25-35 years B.P.

Calcium and Mg concentrations increase in the precultural sediment. On the other hand, Al and K profiles fluctuate with depth of sediment. Unexpectedly, the maximum concentrations of Al, K and Mg are found in the precultural sediment at the 60-90 cm interval.

Lake Minocqua

Profile WC-51. The chemical stratigraphy of Minocqua core WC-51, obtained in 10.7 m of water in the deep-area of the northwest bay is given in Figure 4.17. The sediments consist of a homogeneous brown-black gyttja. The rise in ragweed at the 10-15 cm level separates the pre- and postcultural sediment.

Organic C generally increases with depth of sediment throughout the

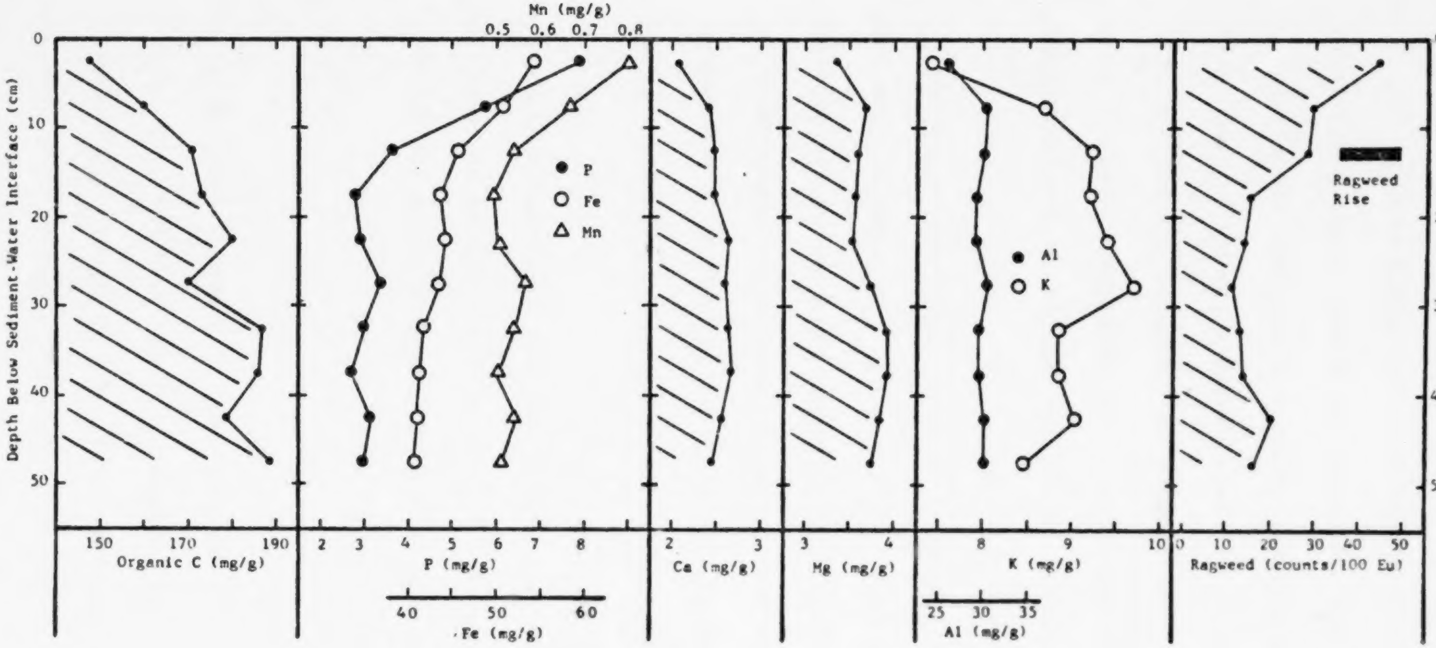


Figure 4.17 Chemical Stratigraphy of Lake Minocqua Profile WC-51, Northwest Bay.

50 cm core, although from the sediment-water interface to the base of the cultural horizon (0-15 cm), organic C concentration increases more rapidly with sediment depth.

Phosphorus, Fe and Mn concentration profiles are closely related and tend to form a mirror image to organic C. In the precultural sediment, P, Fe and Mn remain constant or increase slightly in an upward direction. In the top 15 cm of sediment these elements become enriched. For example, the P concentration increases 2-3 fold in the postcultural deposits over the P found in 35 cm of precultural sediment examined. The increase in P concentration in the upper sediments may be partially attributed to the discharge of sewage from a secondary treatment plant into the northwest bay in 1935-1964.

Calcium, Mg and Al concentrations remain practically constant with depth of sediment. However, K concentration decreases in the top 10 cm of sediment.

Profile WC-52. The chemical stratigraphy of Minocqua WC-52, obtained in 13.7 m of water in the deep-water area of the southwest bay, is given in Figure 4.18. The increase from low to high ragweed counts occurs at the 25-30 cm horizon. Based on the rise in ragweed pollen, the sedimentation rate in the southwest bay, which is fed by an inlet stream, is greater than in the northwest bay. In both Minocqua cores the rise in ragweed coincides very closely with the major changes in chemical stratigraphy.

Organic C concentration remains constant in the precultural sediment below 30 cm and generally decreases upward in the postcultural deposits (30-0 cm). Concurrent with the decrease in organic C concentration most of the other sedimentary components increase in concentration. Thus, it

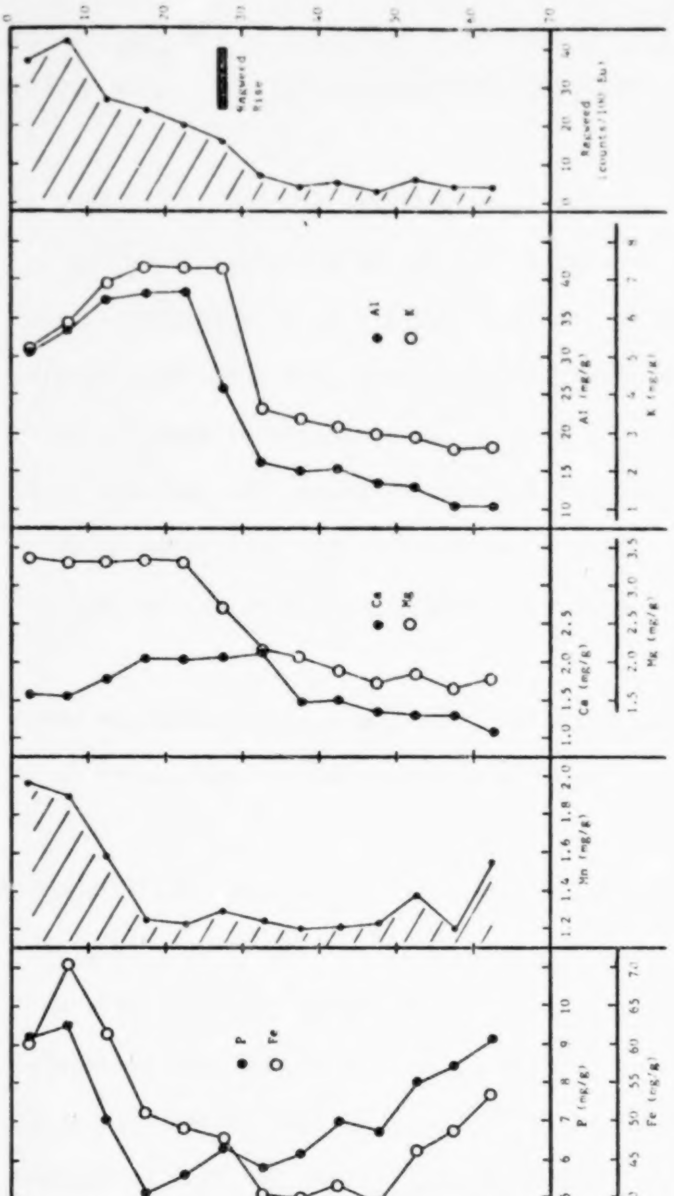


Figure 4.18 Chemical Stratigraphy of Lake Minocqua Profile WC-52, Southwest Bay.

appears that organic C is effected by dilution of inorganic materials.

Phosphorus, Fe and Mn profiles in the southwest bay are not as closely related as that in northwest bay. For example, phosphorus and Mn increase in the top 15 cm of sediment, while Fe increases in the top 30 cm corresponding to the ragweed rise. Maximum P concentrations (8-9.5 mg/g) are found in the top and bottom of the core although the P in the postcultural sediment is accompanied by a proportionally higher Fe and Mn content than in the precultural sediment.

Magnesium, Al and K concentrations increase markedly at the 25-30 cm horizon which corresponds exactly to the initial rise in ragweed pollen.

Calcium concentration remains nearly constant with depth.

The following observations can be made on profile WC-52. First, phosphorus does not increase in the postcultural over the precultural sediment in relation to the increase in Fe, Mn, Al, K, and Mg compounds which should provide a favorable sorption environment for P retention. Livingstone and Boykin (1962) noted that in Linsley Pond high P binding capacity is correlated with high mineral content of the lake mud. Thus, as the rate of mineral sedimentation falls, so does the P content of the mud. It is doubtful the rate of supply of P has decreased in recent times; therefore, the P finally residing in Minocqua sediment may also depend on the rate of loss of P from the sediment to the water phase and the rate of accumulation of the whole sediment. Second, Al, K and Mg concentrations show pronounced changes in the postcultural sediment in southwest bay, whereas these elements remain constant with depth in the northwest bay. Third, both a minimum and maximum P concentration are found in the postcultural sediment.

Weber Lake

The chemical stratigraphy of Weber Lake core WC-66, obtained in the center of the lake, is given in Figure 4.19. The sediment consists of a black-brown organic mud, or gyttja. The most interesting feature of the core is the pronounced fluctuation in chemical composition with depth of sediment. Ragweed pollen increases sharply at the 15-20 cm level which indicates the sedimentation rate of Weber Lake would be relatively low.

Organic C concentration varies from 246-367 mg/g throughout the core; however, the mean concentration of organic C is greater in the precultural deposits than in the upper 20 cm of recent sediment. A large maximum peak of organic C is found deep in the precultural sediment at 55-70 cm.

Phosphorus concentration fluctuates considerably, but within a narrow range of 2.8-3.9 mg/g P. Iron and Mn concentration profiles are not closely related to P as shown for most of the other cores examined. Scientific experimental studies involved the addition of superphosphate to the lake from 1932-1936 to increase the productivity (Potzger and Van Engel, 1942); the annual addition of superphosphate fertilizer to water was as follows: 1932 - 750 pounds; 1933 - 500 pounds and 1934 - 500 pounds. This addition of fertilizer has no observable effect of increasing P concentration in the recent sedimentary column.

Iron concentration (10-11.5 mg/g) remains nearly constant throughout most of the column (10-70 cm), but increases near the top and bottom of the core.

Manganese and Mg concentrations remain more or less constant with depth of sediment.

Aluminum and K concentrations fluctuate widely with depth of sediment

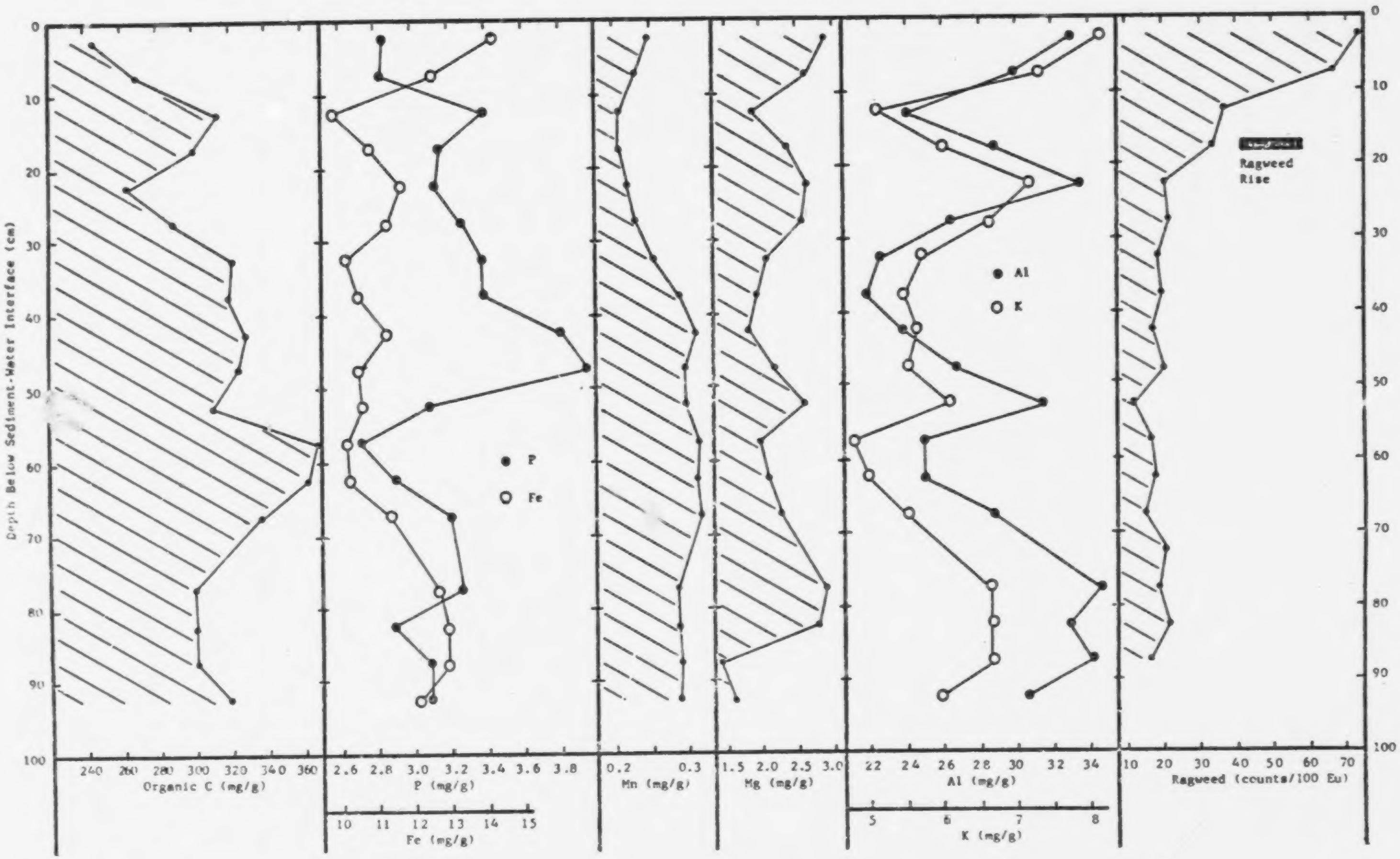


Figure 4.19 Chemical Stratigraphy of Weber Lake Profile WC-66.

although the two profiles show similar distribution patterns. A close inspection of the core sequence reveals that Fe, Al, K and Mg show the same inflections (minimum and maximum peaks) and form a mirror image to organic C. Weber Lake is the only northern Wisconsin lake studied in which Fe appears to be closely related to Al, K and Mg concentration profiles. As a comparison, Fe is always closely associated to the K and Al profiles in the southern Wisconsin calcareous lakes.

The oscillations in the chemical stratigraphy were somewhat unexpected in view of the slow sedimentation rate of Weber Lake. Theoretically, a slow sedimentation rate should allow more time for the mixing of old and new sediment layers thus producing an integrated sediment smoothing out exaggerated peaks. In order for the pronounced peaks to persist the depth of the sediment mixing column must be short.

The overall Weber Lake sediment sequence shows few trends of increasing or decreasing concentrations. The fluctuations may possibly be attributed to changing lake level causing differential leaching and erosion of the shoreline. A small seepage lake, such as Weber Lake, may be affected easily by changing precipitation patterns which may in turn change the lake level.

Little John Lake

The chemical stratigraphy of Little John WC-67, obtained in 5 m of water in the center of the lake, is given in Figure 4.20. The core is about twice the length of most cores obtained from the northern Wisconsin lakes. The sediments were a flocculate brown-black gyttja throughout the 175 cm core. Even though the entire core was fractionated in the field into 5 cm intervals, chemical analyses were performed on every other section below

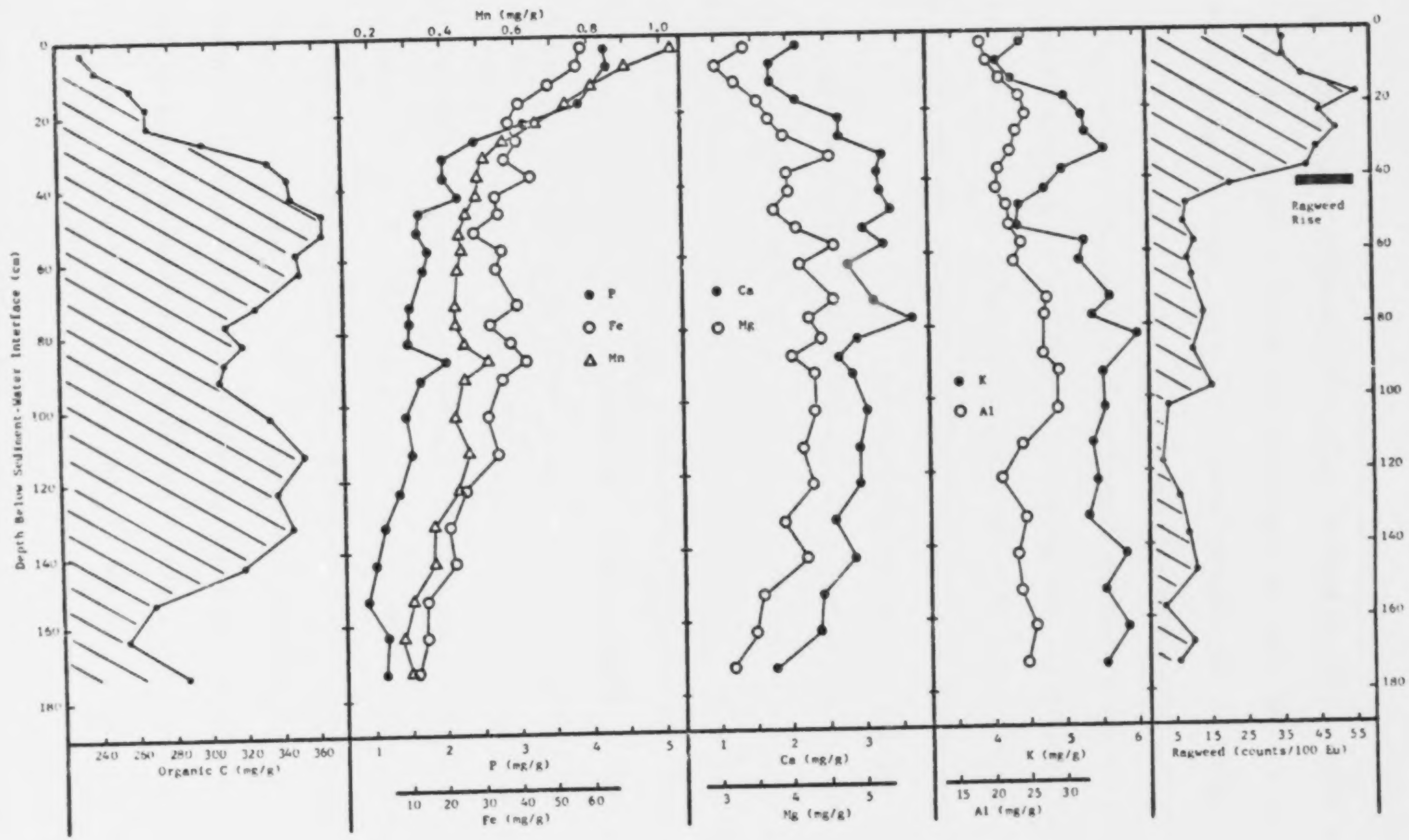


Figure 4.20 Chemical Stratigraphy of Little John Lake Profile WC-67.

100 cm in the core.

Some of the most pronounced changes in chemical stratigraphy correspond to the initial rise in ragweed at the 40-45 cm level. The sedimentation rate based on the ragweed curve for Little John is high compared to most of the northern lakes examined.

Organic C concentration shows a sharp decline above 40 cm to the sediment-water interface. The decrease in organic C is accompanied by an increase in concentration of P, Fe and Mn compounds. In the precultural sediment from 40-150 cm organic C fluctuates between 308-364 mg/g. Below 140 cm the organic C tends to decrease.

Phosphorus, Fe and Mn concentrations increase upward throughout the length of the core; however, above 40 cm in the postcultural sediment, P, Fe and Mn show an accelerated increase. For example, P increases from approximately 1 to 1.6 mg/g in the precultural sediment from at least 300-400 years B.P. to approximately 100 years B.P., then the P concentration increases rapidly from 1.6 to 4.2 mg/g in the postcultural sediment. There is considerable parallelism in the P, Fe and Mn profiles.

Calcium and Mg concentrations remain nearly constant within a range of 1.7-3.6 mg/g and 3-4.6 mg/g for Ca and Mg, respectively. Aluminum and K concentration remain nearly constant and fluctuate within a narrow concentration range throughout the core. Little John Lake is a spring-fed lake with no inlet streams which may account for the fact that the concentration of mineral products containing K and Al did not increase concurrently to changes in ragweed pollen and several chemical components.

Devils Lake

The chemical stratigraphy of Devils Lake core WC-75, obtained in 13.1

m of water, is given in Figure 4.21. The sediments were a greenish-black, unstratified gyttja throughout the 95 cm core. Nothing is known of the thickness of the muds. A marked increase in ragweed abundance occurs at the 10-15 cm horizon.

Organic C concentration generally increases with depth of sediment. It appears that organic C deposition is represented by three trends: (1) constant concentration (95-60 cm), (2) an upward decrease (60-15 cm and (3) an accelerated upward decrease in the postcultural sediment.

Phosphorus, Fe and Mn concentration profiles are similar to each other and form a mirror image to the organic C profile. The top 15 cm of postcultural sediment becomes enriched in P, Fe and Mn while organic C decreases markedly. The initial rise in P, Fe and Mn concentration at the 60 cm level is estimated to be at least 400-600 years B.P. based on the sedimentation rate calculated from the recent rise in ragweed.

Calcium and Mg concentration profiles also develop a double break in stratigraphy forming a mirror image to the organic C profile. The magnitude of change in concentration, however, is only slight with depth of sediment.

The K concentration remains nearly constant with depth of sediment except in the top 15 cm of postcultural deposits where K increases markedly. Aluminum concentration increases generally throughout the entire core, but the most pronounced increase in Al occurs at the 55-60 cm level which corresponds to the early break observed for P, Fe, Mn and organic C concentrations.

Sparkling Lake

The organic C and ragweed profile of Sparkling Lake core WC-65,

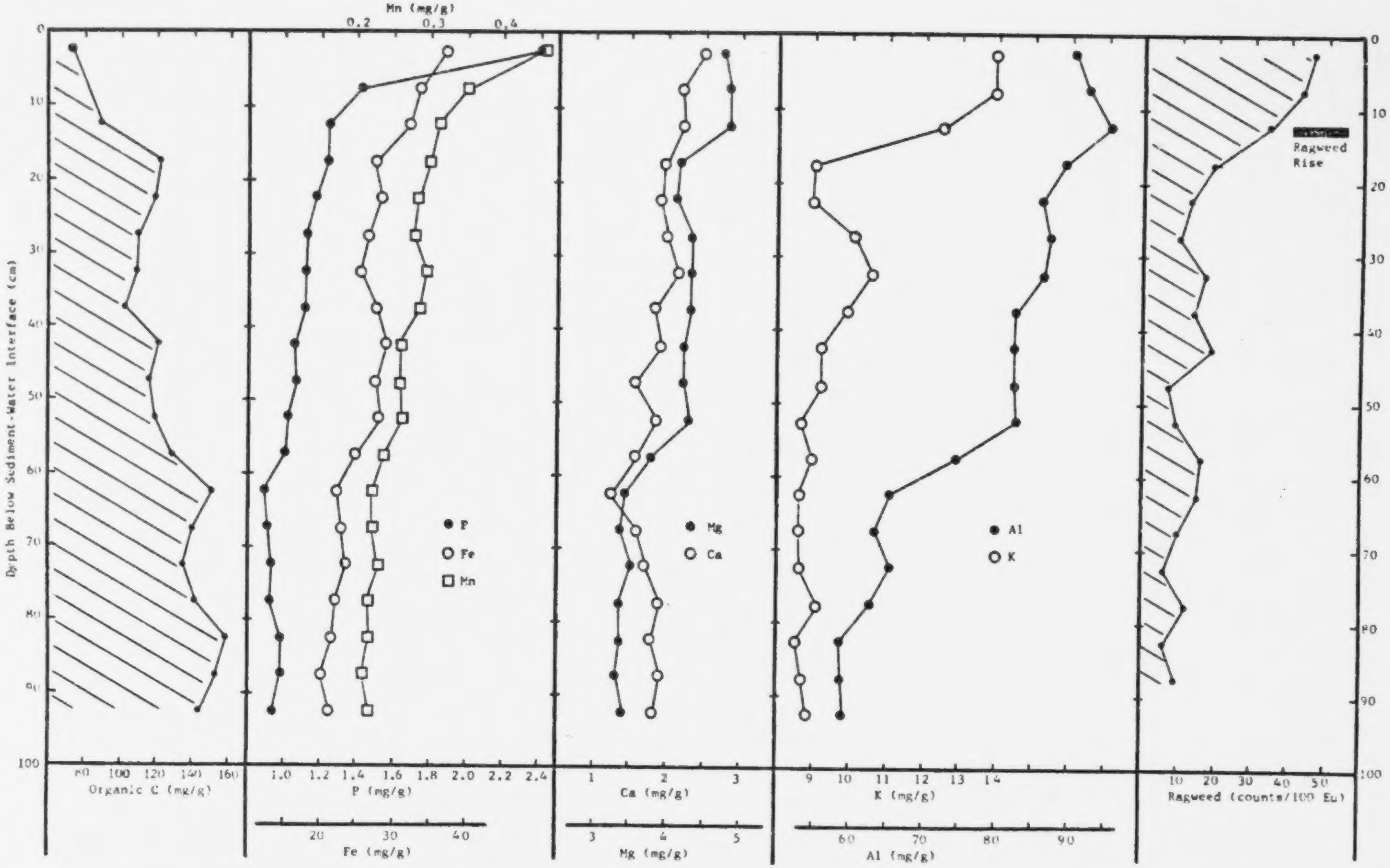


Figure 4.21 Chemical Stratigraphy of Devils Lake Profile WC-75.

obtained in the center of the southern half of the lake, is given in Figure 4.22. The sediment consists of a black-brown organic mud, or gyttja.

The only determinations made on WC-65 were organic C and ragweed pollen counts. Ragweed pollen counts increase sharply at 10-15 cm separating the pre- and postcultural sediment. The ragweed curve indicates the sedimentation rate for Sparkling Lake is low. Concurrent with the increase in ragweed, organic C concentration decreases rapidly (15-0 cm). In the precultural sediment below 15 cm, organic C concentration fluctuates between 225-278 mg/g. But the most dramatic decline in organic C occurs in the postcultural sediment.

Comparison of Mean Concentrations in Pre- and Postcultural Sediments in Noncalcareous Lakes. The mean concentration of various chemical components for pre- and postcultural sediments of Little St. Germain, Trout, Minocqua, Weber, Little John and Devils lakes are shown in Table 4.8. A comparison of the mean concentration of postcultural over precultural sediment is presented as a ratio, *K*, in Table 4.9.

Cores were obtained from separate bay areas in lakes with an irregular shoreline. Considerable differences as well as similarities exist in the mean concentration and the relative change of chemical components in the pre- and postcultural sediment of cores from the same lake.

The cores from Little St. Germain West Bay and South Bay are very similar to each other (accepting 65-70 cm ragweed boundary for South Bay). Both cores show an increase in Al, K, Mg and Ca and a decrease in organic C, P and Mn concentrations in the upper layers of sediment. In West Bay the concentrations of P, Fe and Mn are higher than South Bay throughout

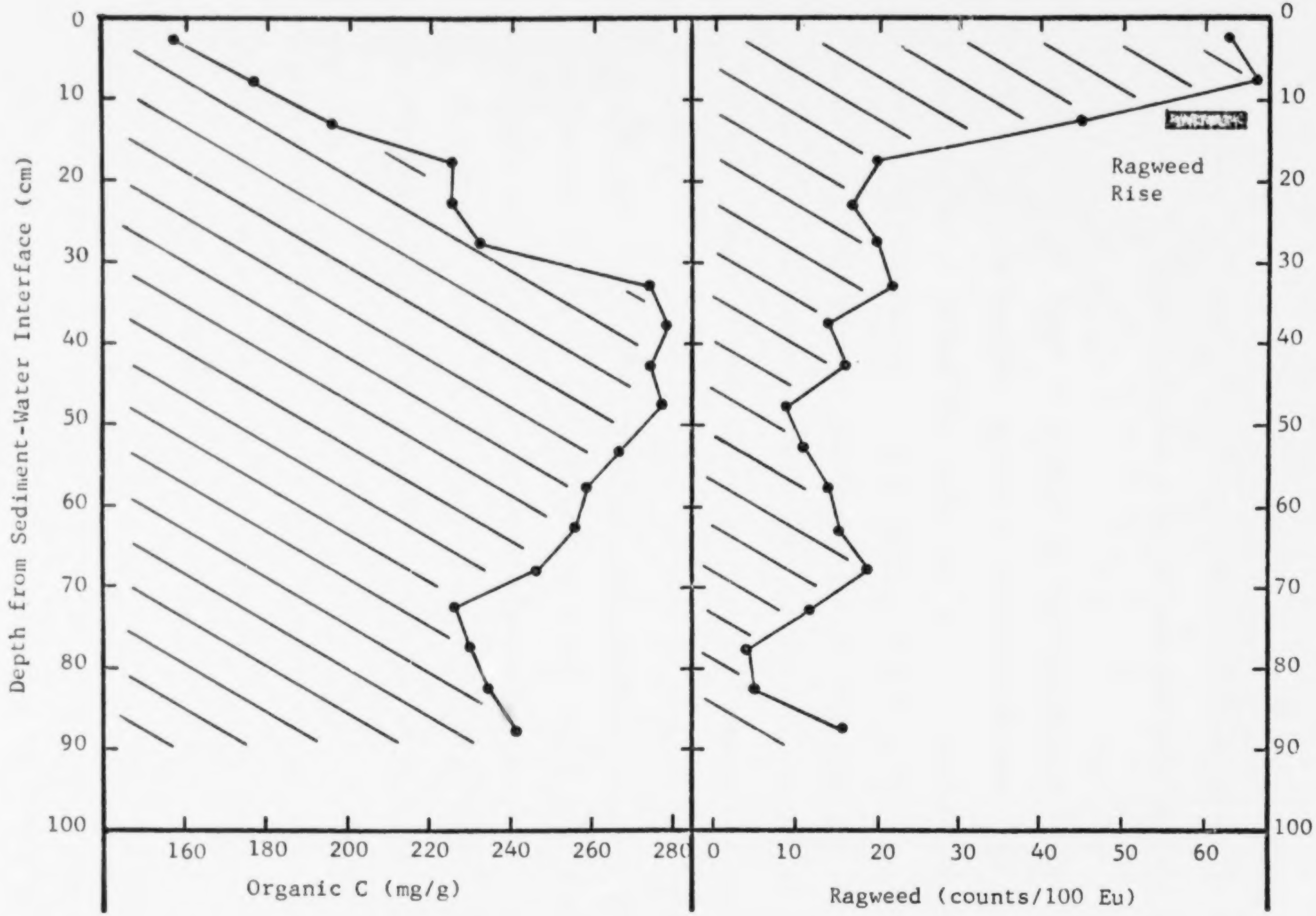


Figure 4.22 Organic Carbon and Ragweed Pollen Profiles for Sparkling Lake Core WC-65.

Table 4.8 Mean Concentration of Pre- and Postcultural Sedimentary Components for Noncalcareous Lakes.

Core		Org-C	P	Fe	Mn	Al	K	Mg	Ca
		mg/g							
Little St. Germain									
W., WC-92	a	145	8.85	89.2	1.27	15.0	3.54	2.44	0.63
	b	217	14.1	96.2	2.34	9.38	2.08	1.63	0.50
* S., WC-56	a	210	6.15	49.5	0.407	16.1	3.64	2.17	1.15
	b	235	10.6	52.3	0.627	9.37	1.54	2.11	0.63
Trout									
N., WC-60	a	145	5.73	52.1	2.35	25.9	4.55	3.24	2.39
	b	223	1.81	40.1	1.23	29.2	4.96	3.75	3.69
** S., WC-59 *	a	155	5.43	55.6	2.69	--	1.33	2.44	3.37
	b	189	4.71	57.2	2.50	--	1.32	2.56	3.72
Minocqua									
S.W., WC-52	a	127	7.33	58.6	1.59	35.6	6.55	3.33	1.80
	b	151	7.24	44.7	1.29	15.0	3.59	1.97	1.54
N.W., WC-51	a	161	5.80	50.4	0.670	28.8	8.45	3.54	2.33
	b	181	3.01	42.3	0.524	29.8	9.08	3.74	2.58
Weber									
WC-66	a	282	3.06	11.9	0.225	29.0	6.64	2.46	0.635
	b	317	3.23	11.3	0.287	28.4	5.95	2.21	0.864
Little John									
WC-67	a	288	3.14	44.9	0.692	22.0	4.86	3.71	2.54
	b	333	1.65	35.7	0.453	25.9	5.21	4.25	3.07
Devils									
WC-75	a	81.0	1.68	34.4	0.372	92.7	13.4	4.81	2.29
	b	129	1.02	24.8	0.247	74.2	9.09	3.84	1.79

[a] Mean concentration of postcultural sediment

[b] Mean concentration of precultural sediment

** $HClO_4$-HNO_3 digestion (w/o HF)

* Mean concentration calculated using 65-70 cm horizon separating pre- and postcultural sediments

Table 4.9 Comparison of Mean Concentration of Postcultural over Precultural Sedimentary Components for Noncalcareous Lakes.

Core	Org-C	P	Fe	Mn	Al	K	Mg	Ca
	$\underline{K}$							
Little St. Germain								
W., WC-92	--	--	0	--	+++	+++	++	++
S., WC-56	0	-	++	0	++	+++	+++	+++
Trout								
N., WC-60	--	+++	++	+++	--	0	-	0
S., WC-59	-	+	0	0	n.d.	0	0	0
Minocqua								
S.W., WC-52	-	0	++	++	+++	+++	+++	+
N.W., WC-51	-	+++	+	++	0	0	0	0
Weber								
WC-66	-	0	0	--	0	+	+	--
Little John								
WC-67	-	+++	++	+++	-	0	-	-
Devils								
WC-75	--	+++	++	+++	++	++	++	++

$$\underline{K} = \frac{\text{mean concentration of postcultural sediment}}{\text{mean concentration of precultural sediment}}$$ (see Table 4.8)

Notation:

$1.1 \geq \underline{K} \geq 0.9 = 0$

$1.1 < \underline{K} \leq 1.2 = +$

$1.2 < \underline{K} \leq 1.5 = ++$

$\underline{K} > 1.5 = +++$

$0.9 > \underline{K} \geq 0.8 = -$

$0.8 > \underline{K} \geq 0.5 = --$

$\underline{K} < 0.5 = ---$

n.d. = no determination

the cores.

In the cores from the North and South Trout Lake, considerable similarity is noted in the order of magnitude of the mean concentration of P, Fe, Mn and organic C in the postcultural sediments. Also as shown in Table 4.9, the K values for K, Mg, Ca are similar for the two Trout Lake cores. The mean concentrations of Fe and Mn are higher in the postcultural than the precultural sediments of North Trout, while Fe and Mn are almost constant with depth of sediment in South Trout. Both Trout Lake cores show a decrease in organic C and an increase in P in the postcultural sediments.

There are probably more differences than similarities in the concentration profiles of the two Minocqua cores obtained from the southwest bay and the northwest bay. The K value for Al, K, Mg and Ca is positive in the southwest bay, which is connected to an inlet stream, and zero in the northwest bay. The relative distribution of P concentration in the postcultural over precultural sediments of the two bays is quite different. In the northwest bay which received sewage effluent directly from the town of Minocqua, the K value is positive, and in the southwest bay the K value is negative. But the sedimentary concentration of P is greater in the southwest bay which is further from the point of sewage discharge than in the northwest bay. The Fe concentration is about the same in sedimentary profiles of the two cores.

Weber and Little John lakes which are seepage and spring-fed lakes, respectively, contain the highest concentration of organic C of the lakes examined in both pre- and postcultural sediments. On the other hand, Weber and Little John lakes contain low P and Fe compared to the other lakes. In Weber Lake the K values are mostly zero or minus; potassium and Mg are the only elements that increase in the postcultural sediment of Weber Lake.

Phosphorus, Fe and Mn are the only elements that show a positive increase in the postcultural sediments of Little John Lake.

In Devils Lake all the constituents except organic C show a positive K value.

A trend which is common to all the northern noncalcareous lakes is an increase of organic C with depth of sediment. With the exception of organic C, in all the noncalcareous lake cores examined, the chemical components do not display a consistent pattern of increasing or decreasing concentration in the postcultural over the precultural sediment. In nearly all the lake cores examined, P, Fe and Mn concentration profiles are closely related both in the pre- and postcultural sediment. The only exceptions to this observation are oligotrophic Weber Lake and the shallow water core from the South Bay of Little St. Germain. A close association of organic C with P, Fe or Mn profiles is found in the Little St. Germain cores only. Generally organic C concentration profiles form a mirror image to P, Fe and Mn.

D. Estimation of Sedimentation Rates Using *Ambrosia* Pollen

The horizon in a core sequence exhibiting a marked increase in ragweed abundance provides an estimation of sedimentation rate as well as an identification of postcultural and precultural sediment deposition. Historical records of deforestation in northern Wisconsin indicate extensive logging commenced during the period of 1850-1870 and increased to peak lumber production by 1899 (Curtis, 1959). Fires swept through the slashings on most lumbered areas creating open lands (Roth, 1898). The southern part of the state was rapidly converted to farm lands by the increasing tide of immigrant settlers. The population of Wisconsin increased from 3,200 in 1830, to 305,000 in 1850 and to 1,315,000 by 1880; in the same intervals, the acreage devoted to crop production increased from about 400,000 to 2,900,000 to 15,300,000 (Curtis, 1959). In order to compute sedimentation rate, one century will be used as the time period since the major disturbance of deforestation and land clearing commenced in Wisconsin. After the time horizon in each of the cores has been identified, the recent rate of deposition can be calculated. This gives an estimation of the average annual deposition since the commencement of cultural activities, as shown in Table 4.10 for calcareous and noncalcareous lakes. The estimated sedimentation rate for most of the noncalcareous lakes ranges from 4.0-4.5 mm/yr to 1.0-1.5 mm/yr. Higher sedimentation rates of 3.5-4.0 mm/yr to 6.5-7.0 mm/yr are observed for the calcareous lakes. The sedimentation rate for the deep-area of Lake Mendota is 3.5-4.0 mm/yr which is the lowest observed for the calcareous lakes. Nriagu and Bowser (1970) found that the first appearance of magnetic

Table 4.10 Estimated Sedimentation Rate in Lake Deposits Based on the Depth of *Ambrosia* Pollen Increase in the Core Column.

Lake	Estimated Sedimentation Rate in Noncalcareous Lakes in Order of Decreasing Rate (mm/yr)	Lake	Estimated Sedimentation Rate in Calcareous Lakes in Order of Decreasing Rate (mm/yr
Little St. Germain, S.	4.0-4.5 (6.5-7.0)*	Wingra	6.5-7.0
Little John	4.0-4.5	Monona (WC-46)	5.0-5.5
Trout, S.	3.5-4.0	Mendota (WC-84)	4.5-5.0
Little St. Germain, W.	3.5-4.0	Mendota (WC-86)	4.0-4.5
Trout, N.	2.5-3.0	Mendota (WC-89)	3.5-4.0
Minocqua, S.W.	2.5-3.0		
Weber	1.5-2.0		
Sparkling	1.0-1.5		
Devils	1.0-1.5		
Minocqua, N.W.	1.0-1.5		

*Secondary rise in ragweed at 6.5-7.0 cm horizon spherules occurred at the 35-40 cm level in deep-water Mendota core. They suggested that these spherules are flue products derived from industrial and domestic activities supplied to the lake through the action of washing the atmosphere or as the detrital load from urban runoff. The ragweed pollen increase corresponds exactly to the level of increase for magnetic spherules in the Mendota deep-water core. Thus, the appearance of these stratigraphic markers indicates the base of the cultural horizon in the Mendota core.

A lake with a fast sedimentation rate should contain a small amount of pollen in the enclosing sediment compared to a lake with a slow sedimentation rate. To test this hypothesis, the mean ragweed count/100 eucalyptus grains (Eu)/cm^3 (wet) was calculated for the postcultural and precultural sediments for each northern lake. These values do not represent absolute counts of ragweed grains but only relative counts to the internal standard of eucalyptus pollen. The mean ragweed counts per cm^3 of wet sediment in the pre- and postcultural sediments are arranged in increasing order in Table 4.11. This order generally concurs with the lakes arranged in order of their decreasing sedimentation rates based on the break in the ragweed pollen profile. If the ragweed counts/cm^3 of mud is high, the pollen is not diluted by a high background matrix of sediment; therefore, the sedimentation rate of the lake should be low. On the other hand, if the sedimentation rate is high, the pollen should be diluted in the enclosing sediment to produce a low ragweed count/cm^3 in the mud. For instance, in both the pre- and postcultural sediment, Weber, Sparkling and Devils lakes contain high ragweed counts in the sediment matrix and show a low sedimentation rate

Table 4.11 Ragweed Counts in Sediment Matrix as a Relative Measure of Sedimentation Rate in Pre- and Postcultural Sediment of Noncalcareous Lakes.

Lake	* Mean Ragweed Count/100 Eu/cm^3 for Postcultural Sediment in Increasing Order	Lake	Mean Ragweed Count/100 Eu/cm^3 for Precultural Sediment in Increasing Order
Little St. Germain, S.	7.25	Trout, S.	0.39
Trout, S.	8.25	Minocqua, S.W.	18.6
Little John	8.34	Little St. Germain, S.	21.7
Minocqua, S.W.	8.85	Little St. Germain, W.	21.8
Little St. Germain, W.	8.91	Little John	23.7
Minocqua, N.W.	10.8	Trout, N.	43.8
Weber	11.9	Sparkling	50.3
Sparkling	15.4	Weber	50.7
Trout, N.	15.5	Minocqua, N.W.	66.3
Devils	32.8	Devils	90.5

* Relative counts of ragweed in sediment matrix based on the formula:

$$\frac{\sum \begin{matrix}\text{ragweed counts/g dry sed.} \\ \text{(in each 5 cm core section)}\end{matrix} \times \frac{\text{g dry sed.}}{\text{1 g wet sed.}} \times \frac{\text{g wet sed.}}{\text{cm}^3\ \text{wet sed.}}}{\text{number of sections in postcultural (or precultural) sediment}}$$

based on the increase of ragweed in the core column. On the other hand, Little St. Germain and Little John lakes which have a high sedimentation rate also contain fewer ragweed in the sediment matrix. Since the relative ragweed counts in the sediment matrix follow expected trends based on the sedimentation rates calculated for various cores, it lends support to the validity of estimating sedimentation rates from ragweed profiles and known historical records.

E. Postcultural Sedimentation Intensity

The profiles presented thus far are concentration-depth curves. Graphs of concentration vs. wet sediment thickness do not give a complete picture of deposition rates because compaction, as well as age, increases with depth. If the thickness per unit time, water content and density of the deposits are known, sedimentation intensity of a chemical component ($mg/cm^2/yr$) can be calculated. This calculation can be made for the postcultural column in each core using the ragweed pollen as an estimate of the thickness of sediments since the onset of the cultural period. To give the rate of sedimentation in units of weight per unit area and time allows a comparison of lakes of differing composition, moisture content and compaction.

Southern Calcareous Lakes. The data for sedimentation intensity of several chemical components are given in Table 4.12 for lakes Monona, Wingra and Mendota. An example calculation of sedimentation intensity of P in Mendota core WC-89, is given in Table 4.13. It should be emphasized that the sedimentation intensity shown for the chemical components may not be representative of the entire lake, but only for the location in the lake where the cores were obtained. For example, the sedimentation intensity of organic C is about 3 times less for the Lake Mendota deep-water core than University Bay core WC-84. The sedimentation intensity of all chemical components investigated is higher in University Bay than the deep-water area of Lake Mendota. Even though the concentrations of P, Fe, Mn and Ca increase with water depth from University Bay to the deep-water area, the deposition rate of these

Table 4.12 Sedimentation Intensity of Postcultural Sedimentary Components for Calcareous Lakes.

Lake	Org-C	P	Fe	Mn	Ca	Mg	Al	K
	mg/cm^2/100 yr							
Mendota * WC-89	526	11.9	151	8.30	800	79.4	268 **	72.2
Mendota WC-86	825	14.0	223	8.45	1130	159	509	128
Mendota WC-84	1698	19.1	342	11.1	1620	289	659	189
Wingra	1137	8.98	127	9.40	3920	157	477	83.6
Monona * WC-46	1184 #	19.2	205	8.84	1600	161 #	396 #	107 #

* $HClO_4$-HNO_3 digestion (w/o HF)

** Assuming mean concentration of Al in postcultural sediments from WC-95

Assuming mean concentration of organic C, Al, Mg and K from entire 105 cm column of WC-101

Table 4.13 Calculation of Sedimentation Intensity of Phosphorus for Lake Mendota Core WC-89.

Interval Depth (cm)	Density (g/cm^3)	Dry Solids Content $\frac{\text{g dry wt.}}{\text{g wet wt.}}$	Interval Length (cm)	Conc. of P $\frac{\text{mg}}{\text{g dry wt.}}$	Wt. of P below Sediment Sfc. (mg/cm^2)	Cumulative Wt. of P below Sediment Sfc. (mg/cm^2)
0-5	1.07	0.111	5	1.79	1.06	1.06
5-10	1.11	0.162	5	1.79	1.61	2.67
10-15	1.11	0.194	5	1.31	1.41	4.08
15-20	1.05	0.190	5	1.64	1.64	5.72
20-25	1.07	0.173	5	1.68	1.56	7.28
25-30	1.07	0.164	5	1.96	1.72	9.00
30-35	1.10	0.161	5	1.74	1.54	10.5
35-40	1.08	0.163	5	1.55	1.37	11.9 *

* Sedimentation intensity of postcultural P = 11.9 mg $P/cm^2/100$ yr

components on a weight per unit area and time basis decreases with water depth. The higher deposition rate of P, Fe, Mn and Ca in University Bay is a function of a greater accumulation of sediment, as shown by the depth of the ragweed profile, and a higher percentage of dry solids in the University Bay cores than in the center of the lake.

Lake Wingra has a low P sedimentation intensity, 8.98 mg P/cm^2/100 yr, compared to 11.9-19.1 mg P/cm^2/100 yr for Mendota and 19.2 mg P/cm^2/100 yr for Monona. The sedimentation intensity of Fe is also lower in Wingra than Mendota or Monona, but the sedimentation intensity of Mn is about the same for all three lakes. The deposition rate of organic C in Wingra and Monona is about 2 times that found for the deep-area of Mendota.

The sedimentation intensity of the chemical components from Monona fall within the range of values found for Mendota.

Noncalcareous Lakes. The sedimentation intensity of the chemical components from the profundal sediments of noncalcareous lakes is shown in Table 4.14. It is difficult to generalize about trends in comparing the sedimentation intensity of the various lakes.

The sedimentation intensity of organic C varies from 159-514 mg/cm^2/100 yr which is lower than the calcareous lakes (526-1184 mg/cm^2/100 yr). There appears to be little relation between the productivity classification of a lake and the sedimentation intensity of organic C.

The sedimentation intensity of P is highest for Little St. Germain (20.5 mg P/cm^2/100 yr) and lowest for the two oligotrophic lakes, Devils and Weber (2.76-4.06 mg P/cm^2/100 yr). The P deposition rates

Table 4.14 Sedimentation Intensity of Postcultural Sedimentary Components for Noncalcareous Lakes.

Lake	Org-C	P	Fe	Mn	Ca	Mg	Al	K
	mg/cm^2/100 yr							
Little St. Germain W. Bay, WC-92	338	20.5	207	2.95	1.46	5.67	34.8	8.21
Trout, N. Bay WC-60	293	11.6	106	4.75	4.83	6.55	52.4	9.20
* Trout, S. Bay WC-59	358	12.6	129	6.21	7.79	5.64	--	3.08
Minocqua, S.W. Bay, WC-52	255	14.7	118	3.20	3.62	6.70	71.5	13.2
Minocqua N.W. Bay, WC-51	159	5.75	49.8	0.664	2.31	3.50	28.6	8.36
Weber	255	2.76	10.8	0.204	0.575	2.22	26.2	6.00
Little John	514	5.59	80.0	1.23	4.52	6.60	39.2	8.65
Devils	196	4.06	83.4	0.900	5.55	11.6	224	32.5

* $HClO_4$-HNO_3 digestion (w /o HF)

of the two Trout Lake cores are similar to each other, but in the two Minocqua cores the sedimentation intensity differs by 2-fold. The deposition rate of P ranges from 2.76 to 20.5 mg/cm^2/100 yr in the noncalcareous lakes. The high end of this range is approximate to the sedimentation intensity of 8.9-19.2 mg P/cm^2/100 yr found in calcareous lakes. However, it is observed the sedimentation intensity of Fe and Mn is always higher in calcareous lakes than noncalcareous lakes.

Dry Sediment Accumulation. Another way to examine sedimentation is to follow the dry matter accumulation through time. The dry sediment accumulated is shown in Table 4.15 for the postcultural sediment from the noncalcareous and calcareous lakes. A comparison is given in grams of dry sediment accumulated below one square centimeter since the onset of the cultural period. The dry sediment accumulated varies from 0.905 to 2.42 g/cm^2 and from 7.15 to 17.2 g/cm^2 for noncalcareous and calcareous lakes, respectively. The postcultural accumulation of dry sediment is approximately the same for the noncalcareous lakes with the exception of Weber and the northwest bay of Minocqua. For the calcareous lakes, University Bay core WC-84 and Wingra have the highest dry sediment accumulation (17.2-16.5 g/cm^2), and the deep-water core of Mendota the lowest (7.15 g/cm^2).

Table 4.15 Dry Sediment Accumulated below One Square Centimeter of Mud Surface Since the Onset of the Postcultural Period.

Lake	Dry Sediment Accumulated in Postcultural Sediments of Noncalcareous Lakes in Decreasing Order g/cm^2	Lake	Dry Sediment Accumulated in Postcultural Sediments of Calcareous Lakes in Decreasing Order g/cm^2
Devils Lake	2.42	Mendota WC-84	17.2
Little St. Germain, W. Bay	2.32	Wingra	16.5
Trout, S.	2.31	Monona WC-46	12.2
Trout, N.	2.02	Mendota WC-86	11.1
Minocqua, S.W. Bay	2.01	Mendota WC-89	7.15
Little John	1.78		
Minocqua, N.W. Bay	0.990		
Weber	0.905		

F. Sorption and Desorption of Added Inorganic Phosphorus to Pre- and Postcultural Sediments

The capacity of lake sediments to retain or release P is undoubtedly one of the important factors which influence the concentration of P in the lake water. The purpose of this laboratory study is to assess the P sorptive characteristics on selected strata representing pre- and postcultural sediments. If the chemical composition of the sediments has changed historically, presumably the P sorptive and desorptive capacity of the sediment will also be influenced.

The sediment capacity for sorption and desorption of P is illustrated in Table 4.16 for a representative pre- and postcultural stratum in calcareous cores and for soil samples in a woodland and cultivated region of the Lake Mendota watershed. Grab sediment samples were taken at a depth of 4-5 inches below the soil surface from the woodland area of Picnic Point and from the cultivated Eagle Heights garden area near Second Point. For all the sediment and soil samples, the percent of the total added P sorbed decreases as the initial level of added P increases. The P desorbed as a percent of the added P sorbed generally increases with higher initial levels of added P. The behavior of the P sorptive complex will depend on variations in temperature, pH, ionic strength and contact time. The samples were shaken for 40 ± 4 hours at ambient temperature in 0.1 N NaCl. The pH and temperature of the solutions are presented with the results.

Lake Mendota. The aerobic sorption and desorption of P indicate the postcultural gyttja is a more favorable sorptive and less favorable desorptive environment for P than the precultural marl. In other words, the sediment which sorbed the most P during the sorption step released

Table 4.16 Sorption and Desorption of Added Inorganic Phosphorus to Pre- and Postcultural Sediments of Calcareous Lakes, Woodland and Cultivated Soil in Lake Mendota Watershed.

Lake	Depth of Sediment (cm)	Added P Sorbed as % of Total Added P				Added P Desorbed as % of Added P Sorbed				Net Added P Sorbed as % of Total Added P **				pH after sorption	pH after desorption	Temperature (°C)
		for Initial P Level (µg P/ml)														
		5	10	25	50	5	10	25	50	5	10	25	50			
*Mendota (WC-89)	5-10	90	66	44	30	2	17	29	27	89	56	34	22	7.8	8.2	24-28
Mendota (WC-89)	70-75	76	37	23	13	42	36	38	47	44	29	14	8	7.9	8.3	
*Wingra (WC-92)	5-10	23	14	10	6	57	57	63	61	12	6	4	2	7.9	8.1	24-28
Wingra (WC-92)	85-90	33	23	16	11	44	41	42	47	19	13	9	6	8.4	8.5	
Monona (WC-101)	5-10	80	67	41	30	18	11	17	18	66	60	34	25	7.9	8.0	28-29
Monona (WC-101)	95-100	63	48	33	23	12	25	26	24	56	37	24	20	8.0	8.1	
Woodland Soil		29	13	8	1	49	58	72	88	15	5	2	0	6.1	6.6	28-29
Cultivated Soil		24	9	3	4	29	61	100	96	17	3	0	0	6.6	6.9	28-29

** Following sorption and desorption steps

* The lowest initial P level for Mendota (WC-89) and Wingra (WC-92) was 2.5 µg P/ml, 40 ml P solution used

the least P during the subsequent desorption. The net sorption (after sorption and desorption) of added P, expressed as a percentage of total added P, is higher for the postcultural sediment than the marl. Thus, it appears that the modern sediment has a greater capacity to retain P than the sediments laid down for a long historical period.

The effect of pH on the sorption of P is shown in Figure 4.23 for Mendota postcultural sediment. The maximum uptake of P occurs at pH 4-6.5. This data is in agreement with MacPherson et al. (1958) who equilibrated P at different pH levels with sediments from several lake types. Maximal uptake of P occurred at pH 5.5-6.5. The $CaCO_3$ buffering of Lake Mendota sediments prevents maximal sorption of P.

Lake Wingra at the lowest level of P added to Wingra pre- and postcultural sediment only 33 and 23 percent is sorbed, respectively, which is about 2-3 times less sorption than observed for Mendota sediments. The sorption and desorption of P indicate the postcultural sediment is a less favorable sorptive and more favorable desorptive environment for P than the precultural sediment. The opposite effect with respect to the pre- and postcultural sediment was observed for Mendota. The capacity of Wingra sediments for P sorption is much less than Mendota even though the marl sediment of Mendota and the top postcultural sediment of Wingra contain approximately the same concentrations of organic C, Fe and $CO_3^=$-C. At the lowest level of added P the net sorption is 19 and 12 percent for Wingra pre- and postcultural sediment, respectively.

Monona. Profile WC-101 of Monona contains entirely postcultural sediment. However, there are differences in the sorptive-desorptive capacity of the 5-10 cm stratum and the 95-100 stratum due to changes

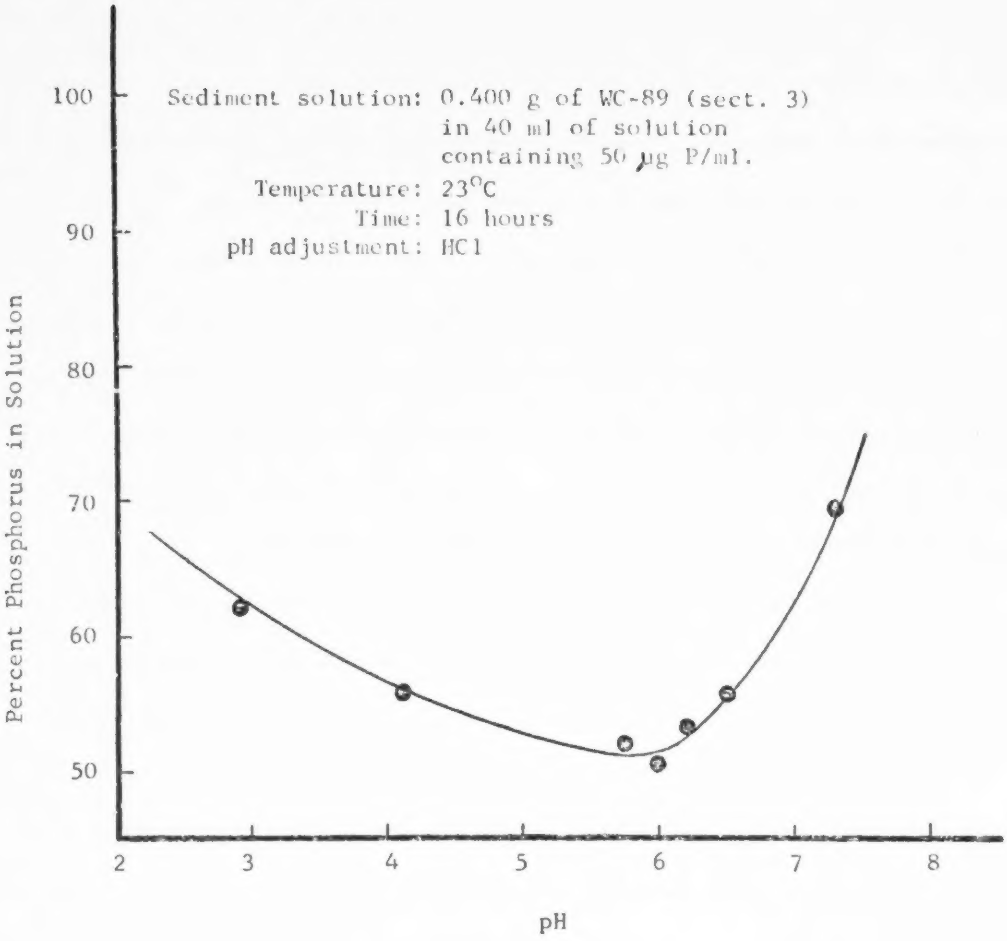


Figure 4.23 The Effect of pH on Phosphorus Sorptive Capacity for a Lake Mendota Sediment.

in the chemical composition of these sediment layers. The sorption and desorption of P indicate the upper stratum is more favorable sorptive and less favorable desorptive environment than the lower stratum. The 5-10 cm level contains more Fe, Al and K than the 95-100 cm level, but the $CO_3^=$-C and organic C concentrations of the two strata are practically equal. The net added P sorbed onto the postcultural sediments is about the same for Monona and Mendota.

Watershed Soils. The P sorptive capacity on both watershed soil samples is less than Monona and Mendota sediments. Phosphorus is desorbed more readily in the acidic watershed soils than the alkaline lake sediments. The pH of the watershed soil solutions range from 6.1-6.9 compared to a pH of 8.0-8.5 for the lake sediment solutions. The difference in P sorptive-desorptive capacity in woodland soil and cultivated soil appears minimal. The chemical characteristics of the watershed soils are shown in Table 4.17. The woodland soil contains more than twice as much organic C as the cultivated soil. The Fe, Al and K concentrations of the watershed soils are the same order of magnitude as found for Mendota sediments; therefore, the large differences in the P sorptive-desorptive capacity of lake sediments and watershed

Table 4.17 Chemical Characteristics of Two Lake Mendota Watershed Soils.

Sample	Org-C	P	Fe	Ca	Mg	K	Al	Mn
	mg/g							
Woodland	48.3	0.88	12.2	1.2	2.3	12.2	45.7	1.35
Cultivated	20.0	0.87	16.9	1.8	4.0	13.7	53.6	1.32

soils can not be accounted for by differences in Fe and Al concentrations. The Ca and organic C concentrations in the watershed soils, however, are considerably less than the Mendota sediments. It appears that the physical and chemical composition of Lake Mendota sediments provide a net sorptive capacity (after sorption and desorption) which is distinctly greater than these two watershed soils.

Noncalcareous Lakes. The sorption and desorption of added inorganic P to pre- and postcultural sediments of noncalcareous lakes is shown in Table 4.18. The pH of the sediment-water solutions vary from 4.6-7.5. In most of the sediment layers examined, the noncalcareous sediments sorb at least 80 percent of the P at the lowest level of added P (5 μg P/ml). The amount of added P desorbed from the sediment is generally less than 10 percent.

Trout Lake. The sorptive-desorptive characteristics of the 10-15 and 100-105 cm horizons of the Trout Lake core are very similar. The Trout sediment sorbs 94 and 89 percent of the P at the lowest level of added P (5 μg/ml) in the top and bottom samples of the core, respectively. The added P desorbed ranges from 4-14 percent. The similar sorptive-desorptive characteristics of the Trout core samples are apparently reflected by the similar chemical composition of the two sediments. For example, the Fe concentrations are 52.5 and 58.4 mg/g for the top and bottom of the core, respectively.

Lake Minocqua. In Minocqua core WC-52, the sorption of added P (5-50 μP/ml) ranges from 98-67 percent in the postcultural sediment to 93-54 percent in the precultural sediment. Although the native P content is about the same in the two sediments, Fe and Al concentrations

Table 4.18 Sorption and Desorption of Added Inorganic Phosphorus to Pre- and Postcultural Sediments of Noncalcareous Lakes.

Lake	Depth of Sediment (cm)	Added P Sorbed as a % of Total Added P (for Initial P Level (µg P/ml))				Added P Desorbed as % of Added P Sorbed (for Initial P Level (µg P/ml))				Net Added P Sorbed as % of Total Added P (for Initial P Level (µg P/ml))				pH After Sorption	pH After Desorption	Temperature (°C)
		5	10	25	50	5	10	25	50	5	10	25	50			
Trout (WC-59)	10-15	94	90	71	54	4	6	10	13	91	84	63	46	5.2	5.2	28-29
Trout (WC-59)	100-105	89	86	65	51	5	7	12	14	88	80	58	44	5.0	5.5	
Minocqua (WC-52)	5-10	98	96	87	67	2	2	5	6	96	95	83	63	5.0	5.7	29-30
Minocqua (WC-52)	60-65	93	80	63	54	3	6	10	13	90	75	57	47	5.5	5.7	
Little John	5-10 15-20	99	98	91	64	21	1.5	4.8	7.6	99	97	87	59	6.8	7.4	27-29
Little John	170-175	49	38	25	16	25	32	36	42	38	29	16	9	6.2	7.5	
Little St. Germain (WC-92)	5-10	100	100	100	98	0.1	0.1	0.2	0.4	100	100	100	98	4.6	4.8	23-29
Little St. Germain (WC-92)	80-85	100	100	100	99	0	0.5	0.1	0.2	100	100	100	98	5.0	5.2	
Devils	0-5	86	70	48	27	7.1	13	18	25	80	61	40	20	6.6	6.8	28-29
Devils	90-95	52	36	22	16	11	22	30	28	47	28	15	12	6.5	6.3	

are higher in the postcultural sediment which probably accounts for the simultaneous increase in P sorption. Although only a small amount of P is desorbed in both sediment types, more P is released in the precultural sediment.

Little John Lake. There is a considerable difference in the sorptive-desorptive capacity of the top and bottom samples of core WC-67. Over 90 percent of the added P(5-25 μg P/ml) is sorbed by the top sample (the 5-10 cm and 15-20 cm sections mixed 1:1 by weight), whereas in the bottom section the sorption ranges from 49-25 percent for the same levels of added P. The Fe content is 4-5 times and Mn about 3 times greater in the top than the bottom core sample. On the other hand, organic C and Al concentrations are greater in the precultural sediment. The dominant influence in determining the P sorptive capacity appears to be the Fe and Mn concentrations.

Little St. Germain Lake, West Bay. The net sorptive capacity of P is 98-100 percent at all levels of added P for both the bottom and top samples of Little St. Germain. The desorption of P is less than 1 percent. The high sorptive capacity of P is attributed to the high Fe concentration ($>$100 mg/g) in both sediment samples. Even though there is high iron in both the pre- and postcultural sediment of Little St. Germain, the native P concentration is greater in the precultural sediment.

Devils Lake. The net sorption of added P (5-50 μP/ml) ranges from 80-20 percent in the top sediment (0-5 cm) to 47-12 percent in the bottom sediment (90-95 cm). The more favorable sorptive and a less favorable desorptive environment of P in the postcultural sediment appears to be associated with high concentrations of Fe, Al, K, Mg and Mn compared to the precultural sediment.

G. Aerobic Leaching of Nitrogen and Phosphorus from Lake Mendota Pre- and Postcultural Sediment.

Core samples of Lake Mendota wet gyttja (0-30 cm) and marl (65-85 cm) were placed in 20 l of distilled water and continuously mixed and aerated. The wet sediments were equivalent to 65.5 g of oven dried mud (105°C). The results of the aeration studies in which conductance, pH, alkalinity, soluble P and inorganic N were followed for a maximum period of 58 days are shown in Figure 4.24 and 4.25 for pre- and postcultural Lake Mendota sediments, respectively. Since the sediments are mixed with a distilled water medium, an increase in dissolved N and P would be expected as the sediment-water mixture equilibrated. However, the important observations will be the relative amounts and rates of N and P released from the pre-and postcultural sediments.

The chemical properties of the sediment before leaching are shown in Table 4.19. The data is typical of chemical composition for the Mendota cores presented previously.

Table 4.19 Chemical Characteristics of Lake Mendota Pre- and Postcultural Sediments Used in Aerobic Leaching Study.

Sample	total C	organic C	P	Fe	Mn	Ca	Mg	Al	K
	mg/g								
Postcultural gyttja	110	86.6	1.83	19.9	1.0	93.0	16.5	45.5	9.40
Precultural marl	129	81.0	0.91	8.3	0.40	192	12.0	10.0	1.80

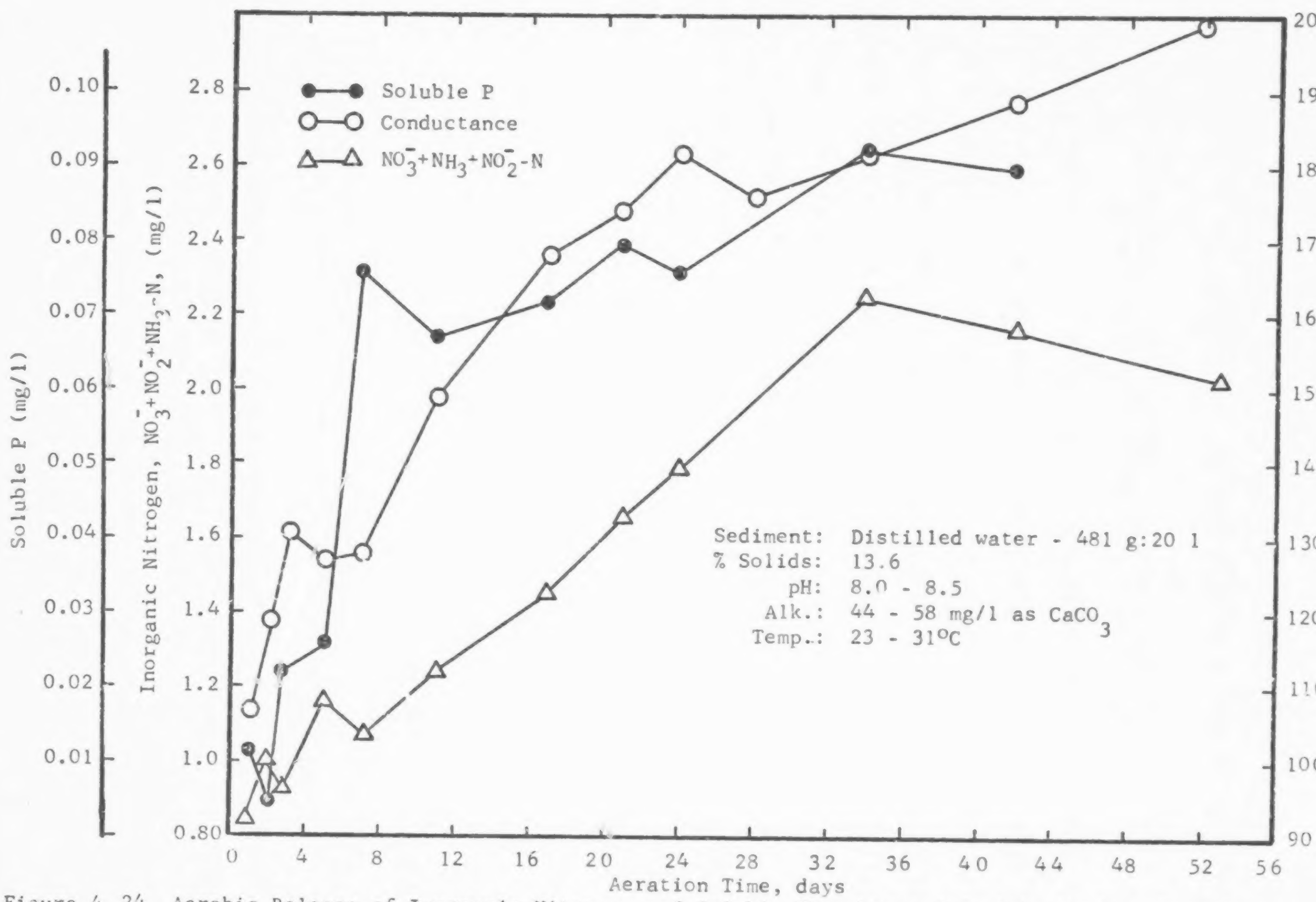


Figure 4.24 Aerobic Release of Inorganic Nitrogen and Soluble Phosphorus from Lake Mendota Precultural Sediment.

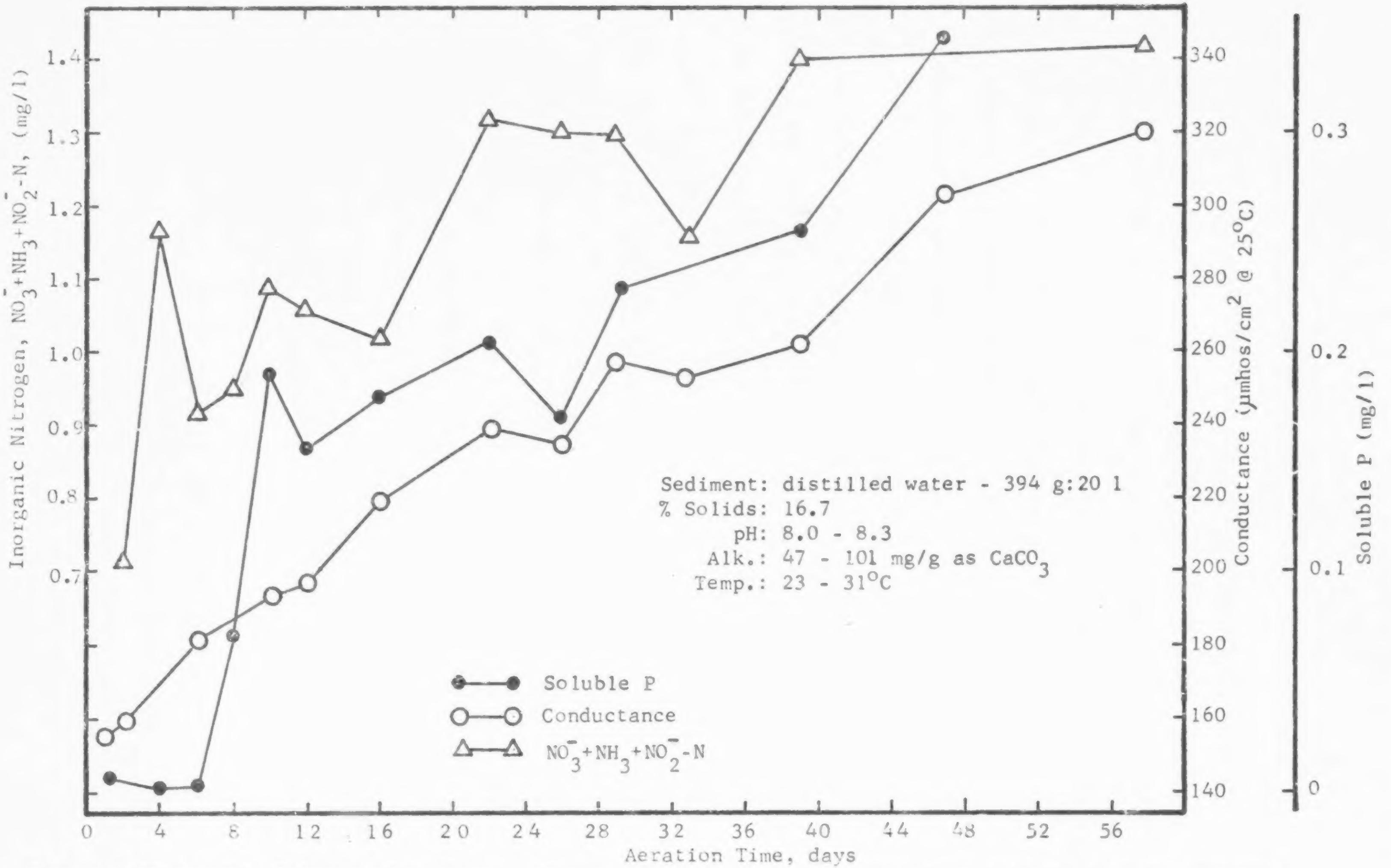


Figure 4.25 Aerobic Release of Inorganic Nitrogen and Soluble Phosphorus from Lake Mendota Postcultural Sediment.

Leaching of Precultural Sediment. The data reported in Figure 4.24 show a general increase in soluble P (0.005-.09 mg/l) throughout the 42 day aeration period. The initial concentration of 0.83 mg/l $NO_3^- + NH_3 + NO_2^-$-N increases to 2.3 mg/l in 36 days. After the 24-day sampling period, $NO_3^- + NH_3 + NO_2^-$-N concentration appears to level off at 2.0-2.3 mg/l. Throughout the 53 day sampling period conductance steadily increases from 107 to 200 µmhos/cm^2 at 25°C. Concurrently, alkalinity increases from 44 to 58 mg/l as $CaCO_3$ (curve not shown).

Leaching of Postcultural Sediment. A general increase is observed for soluble P, $NO_3^- + NH_3 + NO_2^-$-N and conductance during the aeration period as shown in Figure 4.25. For the first 6 days soluble P concentration remains at a low level of 0.004-0.009 mg P/l. From the 6-day to the 47-day sampling period soluble P concentration increases from 0.004 to 0.34 mg/l. After 47 days there is no evidence that P concentration levels off. After the second day $NO_3^- + NH_3 + NO_2^-$-N concentration fluctuates throughout the aeration period at 0.92-1.4 mg/l. Throughout the 56 day sampling period conductance increases from 158 to 320 µmhos/cm^2 at 25°C. At the same time, alkalinity increases from 47-101 mg/l $CaCO_3$ (curve not shown).

Comparison of Pre- and Postcultural Sediment. The initial and final concentrations of inorganic N in the supernatant water from the marl sediment is higher than in the leachate from the gyttja sediment, the increase in concentration of the leachate per day is twice as great in the marl as the gyttja sediment. On the other hand, after 10 days the soluble P concentration in the leachate from the gyttja is 2-4 times greater than in the marl leachate, and the increase in concentration of P in the leachate per day is 3 times as great in the gyttja as the marl sediment. However, the amount of P which is potentially leachable is greater in the gyttja since the concentration of P in the starting material is twice that of the marl. Nevertheless, the gyttja releases a greater proportion of the total P to the water phase than the marl. A close inspection of the release curves shows that the gyttja sediment do not respond until 6 days to a significant release of P, whereas the marl sediment releases P very rapidly from the 2nd day to the 6th day. After 8-10 days the gyttja and marl sediments both released P slower than the initial rise.

The conductance and alkalinity of the gyttja sediment supernatant are also higher than the marl sediment throughout the aeration period. But the leachate from the marl was always a yellow color, whereas the leachate from the gyttja was generally colorless. Iron in the leachate was not detectable with the orthophenanthroline test, and Al and Mn were not detectable with atomic absorption.

It appears that in a intensely aerated system the pre- and post-cultural sediments of Lake Mendota are capable of releasing N and P to the water. It is not known to what extent biological mechanisms have influenced the release rates.

CHAPTER V

DISCUSSION

The purpose of this chapter is to discuss these results in comparison with previously reported work of others and also to discuss aspects and implications concerning the study which could not be conveniently presented in Chapter IV. The major framework of this study involves the observation and interpretation of the chemical stratigraphy of the sediments from calcareous and noncalcareous lakes in southern and northern Wisconsin, respectively. By comparing and contrasting the core profiles from the same geologic and geographic regions, certain conclusions can be made concerning chemical sedimentation in lakes, particularly in regard to the effects man and his civilization have had on the lakes and recent lake deposits. Lake Mendota was the principal study environment and served as the primary source of information.

A. Distribution of Carbon

Several investigators have examined the distribution of organic C with sediment depth in order to measure trends in historical aquatic productivity (Mackereth, 1966; Gorham, 1961; Hutchinson and Wollack, 1940; Horie, 1966). Often the organic C profile has been used to explain lake succession from oligotrophic to eutrophic conditions.

To discuss the factors believed to be controlling the deposition of organic C, a review of various possible methods of organic C deposition in lakes is necessary. The primary factors controlling the abundance of organic C in the sediments are 1) production of organic C of autochthonous origin, 2) sedimentation of allochthonous organic matter, 3) destruction of organic material by organisms or nonbiological processes and 4) variation in deposition rate of whole sediment. It is important to remember that the concentration and the rate of deposition of organic constituents in sediments are the result of differences between rates of formation and decomposition. Sediment trap studies by Kleerekoper (1953) show at least 70-90 percent of the organic matter synthesized in a column of lake water is decomposed prior to incorporation in surface sediments. This does not take into account further breakdown within biologically active surficial zone of sediments. Nevertheless, Mackereth (1966) and Hutchinson and Wollack (1940) believed that the organic matter which becomes incorporated below the biologically surface-active layers of the English Lakes and Linsley Pond reaches a state of considerable stability towards further oxidation shortly after burial. The lignin content of the gyttja from several cores in Trout Lake was determined by Twenhofel et al. (1945). They had anticipated that bacterial decomposition would have led to a decrease in the nonligneous materials, and thus an increase in ligneous materials with depth. Twenhofel et al. (1945) concluded that the fact such a decrease was not observed suggested that bacterial activity ceased in the organic sediments of Trout Lake shortly after burial. Thus, the final concentration of organic C in the sediments will probably depend primarily on factors (1), (2) and (4) mentioned above.

Calcareous Lakes. In the Mendota cores the organic C content remains nearly the same in the pre- and postcultural sediment, but the organic C concentration in the Wingra sediments decreases in the postcultural over the precultural sediment. In the Monona core the organic C concentration (86-107 mg/g) in the postcultural sediment is in the range of the Mendota and Wingra sediments, but the core depth was not sufficient to penetrate the precultural deposits. The observed variation in the organic C content in the cores from Wingra, Monona and Mendota is probably best attributed to the combined influence in the rates of carbonate C, organic C and inorganic sedimentation since the onset of extensive agricultural and urban activities in the Lake Mendota watershed.

Some insight into the relative importance of the sedimentation of carbonates, organic and inorganic material may be gained from Murray's (1956) studies on Lake Mendota. The relationship of gyttja to marl as suggested by Murray (1956) may be considered from the three possibilities: 1) the gyttja is a diagenetic precursor of the marl, 2) the gyttja is developed by leaching of the marl and 3) the gyttja and marl are separate sedimentary units developed under different limnologic conditions. Twenhofel (1933) postulated that the black gyttja was a diagenetic precursor of the marl and that the process of change was one of removal of organic matter by bacteria and precipitation of $CaCO_3$ at depth in the gyttja, thereby the gyttja was converted to marl. Twenhofel based his conclusion that the gyttja was a preliminary product in the production of marl on the assumption that the color of the gyttja resulted from the disappearance of organic matter with depth to produce the light marl. This study shows that the mean concentration of organic C in the pre- and postcultural sediment is essentially constant or increases slightly in the postcultural sediment of Mendota cores. Furthermore, Murray (1956) argues that it is doubtful the gyttja might have resulted from alteration of the marl by removal of carbonate since the deeper stagnated waters would be expected to develop leaching conditions first and thus to a greater degree retain a lower carbonate content. But in fact, the carbonate content is greater, the deeper the water (Murray, 1956). Murray thus concluded the gyttja is simply the most recent sedimentary unit to be deposited in the lake. According to Murray, the fact that the gyttja is a universal deep-water sediment resting not only on marl but on other varied sediment types suggests that it is a unit in itself. The abrupt change in sedimentation from marl to gyttja was explained by Murray as being the result of increasing rates of clastic and organic matter sedimentation superimposed on a constant carbonate depositional pattern. The reported (Murray, 1956) knife-sharp nature of the contact between gyttja and marl was not observed in any of the cores used in this study. In all the core sections examined, the gyttja passed gradually into the marl zone marked by a gradual lightening of color. Apparently the false impression of a knife-sharp contact was created by either compression of the core sections during sampling or the manner of fractionating the core column.

An inspection of the organic C concentration profile of the Mendota long core provides further insight into the historically changing depositional process. The organic C concentration ranges from 59 to 77 mg/g over the core interval 62-900 cm. There is no overall decrease in the organic C content, so diagenetic transformation of the organic matter is probably not an important process. The uniformity of the marl muds suggests that conditions were very uniform throughout the period of its formation; this deposit appears to represent a long period of equilibrium conditions which took place at some unknown time after the final disappearance of the glacial influence. Since the entire depth of the postglacial column is not represented (glacial till not found in substratum), an estimate of the precultural sedimentation rate is lacking. However, the depth of the marl sediments from Cedar Bog Lake, Minn. may provide a rough estimate of a long term sedimentation rate expected in a hard-water lake in an edaphic region similar to Lake Mendota. Lindeman (1941) found the postglacial marl sediments to be 12 m in the deepest part of this hard-water eutrophic lake. If it is assumed that the depth of the Mendota deposits is 12 m, or no more than 1.5 times this depth, the sedimentation rate of the postglacial deposits is in the order of 1.0 to 1.5 mm/yr. This calculation is based on a date of 12,000 years B.P. since the readvance of the Lake Michigan ice lobe (Cushing, 1967). The estimated sedimentation rate of 1.0 to 1.5 mm/yr may be an overestimation. Ogden (1967) calculated a sedimentation rate of 0.43 mm/yr for the early postglacial period and 0.61 mm/yr for the late postglacial period of Silver Lake, Ohio, a hard-water lake. Serruya (1969) found an overall sedimentation rate of 0.91-1.0 mm/yr (8000 years B.P. to present) in Lake Geneva, Switzerland, a drainage lake containing 30-40 percent $CaCO_3$. From the organic C, percent solids and density values of the marl sediments of the long Mendota core and the estimated sedimentation rate of 1.0 to 1.5 mm/yr, the sedimentation intensity for organic C can be calculated and is equal to 117-175 $mg/cm^2/100$ yr. This value is 3-5 times less than the postcultural deposition rate of organic C deposited in the center of the lake. The postcultural increase in organic C represents both an increase in supply of autochthonous and allochthonous organic matter. If the bottom waters and muds have become more reducing since the advent of domestic drainage to the lake, the perservation of organic matter is favored. Belcher and Fogg (1964, as quoted by Brown, 1969) reported that eutrophy and the associated hypolimnetic deoxygenation were considered as major factors in favoring the preservation of pigments in cores from Windermere and Ennerdale Water. A rapid rate of sedimentation would also favor the preservation of organic C, since the period of time during which the organic substance is in contact with the oxygen-bearing bottom water is reduced before being buried. Thus, a portion of the increase in organic matter in Mendota postcultural sediments may be the result of anaerobiosis favoring preservation of organic molecules and a more rapid rate of sediment accumulation. However, there are some compounds, such as DDT, which only breakdown under anaerobic conditions (G. Fred Lee, Personal Communication, 1970); therefore, the overall effects of anaerobic conditions on the breakdown of organic compounds are not known.

The carbonate C profile of the Mendota long core indicates uniform deposition has occurred in the geological past. The constant deposition is interrupted during the cultural period to depress the carbonate C concentration. Calcium carbonate precipitation initiated by planktonic photosynthesis or physico-chemical precipitation has probably not decreased in recent times as inferred directly by the concentration profile of Ca. If photosynthetic uptake of carbon dioxide is the dominant mechanism for carbonate precipitation, then an increase in $CaCO_3$ precipitation in recent times might be slightly favored with increased productivity. However, increased biological respiration, bacterial activity and chemical oxidation serve to decrease $CaCO_3$ precipitation.

Furthermore, Megard (1969) noted that it is unlikely the productivity during the history of lakes can be inferred from the concentration of carbonate in the sediment because a large proportion of the carbonate formed in the epilimnion of productive lakes is dissolved in deep water during periods of stratification. It appears that the most likely explanation for the postcultural decrease in carbonate C concentration is the masking of a somewhat constant (or increasing) carbonate deposition by the increased inorganic sedimentation.

The net effect of the cultural activities in the Mendota basin has been to produce an increase in organic C and inorganic materials in somewhat the same proportion. An increase in inorganic sedimentation is evidenced by the increase in Fe, Mn, K, Al and P in the upper sediments. If the organic C sedimentation rate was not high, it would be reflected as a decrease in the concentration depth diagram the same as $CaCO_3$. The postcultural sedimentation intensity for organic C is 1.6 and 3.2 times greater in University Bay cores WC-86 and WC-84, respectively, than in the deep-water core. The high organic C deposition rate in University Bay is attributed to the proximity of University Creek inlet and the high production of aquatic weeds in the shallow area of the lake. Both of these sources undoubtedly supply allo- and autochthonous organic detritus to the lake. The postcultural sedimentation intensity of organic C in Wingra and Monona is 2.2 times greater than the deep area of Mendota. If the supply of allochthonous organic matter is the same for Mendota and Monona, the higher organic C deposition rate could also be a reflection of the smaller Monona bottom area as well as a greater internal production of organic matter. The evidence would seem to indicate internal production of organic C is quite high in Wingra since the lake does not receive agricultural runoff which would probably contribute heavily to the allochthonous organic C fraction.

Noncalcareous Lakes. The postcultural intensity of organic C varies from 159 to 514 mg/cm^2/100 yr which is lower than the calcareous lakes (526-1184 mg/cm^2/100 yr). However, the concentration of organic C is much greater in the noncalcareous lakes. The highest organic C deposition rate is observed for Little John, a shallow, spring-fed, eutrophic lake, and the lowest organic C deposition rate is shown in the northwest bay of Minocqua, a eutrophic drainage lake. Thus, there is not necessarily any relationship between the productivity classification of a lake and the absolute amount and rate of accumulation or organic C in the postcultural sediments.

In all of the noncalcareous lake cores examined with the exception of South Bay of Little St. Germain, the highest organic C content occurs in the precultural sediments and decreases upward in the postcultural sediment. Often the decline of organic C concentration is contemporaneous with the rise in the ragweed pollen. The decrease in organic C is usually accompanied by an increase in Fe and Mn and/or Al, K, Ca and Mg concentration. Both K and Al are associated with the mineral fraction of the sediment. Mackereth (1966) demonstrated the near linearity of the relationship between the mineral content of the sediment and the Na-K concentration. The concentration of Al and K (and other associated elements) in the sediment may be regarded as being directly proportional to the intensity of erosion. If the rate of organic C deposition remains constant and the rate of inorganic sedimentation increases, the percentage of organic C will decrease. The cores from South and West Bay of Little St. Germain, the southwest bay of Minocqua and Devils show clear evidence of increased Al, K, Mg and Ca concentration in the post-cultural over the precultural sediment concurrent to the decline in organic C concentration. A close inspection of the Weber Lake core sequence reveals that Fe, Al, K and Mg show the same inflections (a minimum and maximum peaks) and form a mirror image to organic C. If it is assumed the biological productivity of oligotrophic Weber Lake has not increased or decreased throughout its history as represented by 1 m of sediment, the changes in the organic C profile are then inversely proportional to the inorganic sedimentation rate.

Hutchinson and Wollack (1940) observed in Linsley Pond a considerable decrease in organic and an increase in inorganic content in the most recent unconsolidated sediment at the top of the profile, as compared to the levels immediately below. It was assumed by Hutchinson and Wollack that the organic production in the lake remained constant, but the rate of silting of the present mud was 2.6 times that occurring before the human agency became prevalent in the 18th century. Similarly, a drastic reduction in the percentage of organic matter occurred in the upper 20 cm of a core from Potato Lake, Arizona(Whiteside, 1965). Whiteside (1965) explained that the transport of inorganic materials and its deposition in the upper sediments were increased due to logging and grazing activities in the lake basin. The lacustrine record of Ennerdale, Windermere and Esthwaite, England show either insignificant change or an increase in organic matter concentration near the tops of cores representing deposits following the development of a fairly dense human settlement on the lake shores (Mackereth, 1966; Pennington, 1943). In Lake Washington, near Settle, Edmondson (1969) observed that the organic matter characteristically increases in the top 15 cm (representing approximately 40-50 years). Although the concentration of organic matter varied in Lake Washington within different parts of the lake. Edmondson felt in general either the lake laid down richer organic sediments or else decomposition was less during the era 1916 to 1958 than before.

In South Trout, North Trout, West Bay of Little St. Germain, in the northwest bay of Minocqua, Weber and Devils the organic C shows a slight upward decrease before the postcultural period is initiated. It appears that either a general increase in inorganic sedimentation rate or a decrease in production of organic matter has occurred before the major cultural influence from deforestation in the above named lakes. The decline in organic C near the tops of the cores is often rapid, but the influences causing the change in the physical and chemical environment before the cultural period are exemplified by gradual decrease in organic C, perhaps indicating a climate episode. There is evidence of a cold climate, "little ice age", during the period 1430-1850 A.D. (Lamb, 1963). A climate change may have influenced rates of erosion or lowered the organic production in the lake prior to 1850 assuming the average temperature of the water to be colder and the water levels higher than post 1850. It seems unlikely, however, that mean temperature departures from present-day conditions were sufficient enough during this epoch to produce a detectable difference in organic C production in these lakes. If the decline in organic C is accompanied by an increase in Fe and Mn and/or Al, K, Mg and Ca, the mechanism causing the decrease in organic C before the cultural period is probably an increase in inorganic sedimentation.

In summary, it appears that the organic C concentration depth profiles have been modified by cultural activities in the noncalcareous lakes. This is marked almost always by a trend towards decreasing concentrations of organic C in the postcultural column. The primary controlling factor in determining the final organic C concentration appears to be the rate at which the sediment as a whole is deposited. The rate of sedimentation appears to be inversely proportional to the organic C content.

B. Distribution of Nitrogen

Organic N determined by the Kjeldahl method was performed on cores from lakes Mendota (WC-89), Wingra (WC-92) and Trout (WC-59). The distribution range of organic N is 5.7-10.0 mg/g, 6.6-10.6 mg/g and 13.8-18.4 mg/g for Mendota, Wingra and Trout cores, respectively. In soils and lake sediments organic N is the dominant form usually ranging from 95 to 98 percent of the total N (Bremner, 1965; Keeney et al., 1970) and is a function of the amount of particulate organic matter deposited (Bortleson, 1968). After deposition, the organic N-containing compounds are modified by biological agents, chiefly bacteria, with the liberation of part of the N in soluble forms. One of the most striking features of the data is the close association between organic C and organic N curves; in the three cores examined, almost every irregularity in the former is reflected in the latter. Since organic C and organic N concentrations show considerable association, the conclusions that were reached concerning organic C depth profile patterns would also apply to organic N distribution. Therefore, it would seem that there is little or no relationship between the productivity classification of a lake and the sedimentary concentration or intensity of organic N. However, Keeney et al. (1970) pointed out from their sampling of northern Wisconsin lakes, that the organic N content of sediments from eutrophic soft-water lakes was much higher than from those lakes of lower fertility.

Carbon-Nitrogen Ratio. The organic C to organic N ratio with depth of sediment for the three cores examined is shown in Table 5.1. The C/N ratio fluctuates somewhat with depth of sediment in each of the cores; in the Trout Lake core there is a trend of increasing C/N ratio with

Table 5.1 Organic Carbon to Organic Nitrogen Weight Ratio for Lakes Mendota, Wingra and Trout Cores.

Depth of Sediment (cm)	Mendota (WC-89) C/N	Trout, S. (WC-59) C/N	Wingra (WC-92) C/N
0-5	7.38	8.85	8.56
5-10	8.85	9.36	9.04
10-15	8.80	9.02	9.95
15-20	8.32	10.2	9.56
20-25	9.69	10.1	9.05
25-30	8.89	10.2	7.82
30-35	8.68	10.6	8.19
35-40	7.22	10.4	8.65
40-45	8.61	10.6	9.95
45-50	7.90	10.3	9.85
50-55	9.98	10.6	8.46
55-60	9.63	10.7	9.37
60-65	11.4	10.7	8.36
65-70	8.00	11.4	8.50
70-75	6.70	11.4	8.68
75-80	7.95	11.6	8.07
80-85	8.07	11.3	7.90
85-90	8.51	11.8	8.34
90-95	8.50	11.1	--
95-100		11.2	--
100-105		10.3	--
C/N (mean)	8.55	10.5	8.79

increasing depth. In lakes Mendota, Wingra and Trout, respectively, the mean C/N ratio for the entire core is 8.55, 8.79 and 10.5. It is noticed that the average C/N ratio is smaller for the two hard-water eutrophic lakes than Trout Lake. The C/N ratio in these sediments is considerably higher than the C/N ratio of approximately 5.7 for plankton (Emery and Rittenberg, 1952), so the organic material must undergo much decomposition releasing N faster than C as it settles through the water column and shortly after it reaches bottom. The increase in the C/N ratio with depth in the Trout core indicates further decomposition of N-containing compounds with aging. The smaller C/N ratio in the top 15 cm of the Trout core may indicate the full mineralization and stabilization of the organic matter has not developed. Arrhenius (1950) presented results indicating that C/N decomposition conditions are influenced also by the dilution of organic matter with mineral matter in such a way that a high dilution will favor a preservation of organic matter in its nitrogen rich state. This may partially account for the low C/N ratio in the calcareous lakes where the sediment accumulation (based on dry weight) is much greater than Trout Lake. According to soils literature, under ordinary circumstances when the C/N ratio of soils is low, the supply of readily available energy material is limited, resulting in slow mineralization of nitrogen (Stevenson, 1964). Such an arrangement is advantageous in that the main N reserves of soil are held in an insoluble form which cannot be leached away but which can be slowly mineralized to support plant growth (Stevenson, 1964). The mineralization of N from fresh organic residues is dependent on a number of physical and chemical conditions of the soil. For example, according to Stevenson (1964) the adsorption of organic N compounds, particularly proteins on clay colloids, has a distinctively protective effect. Based on the foregoing comments, the implication may be that Mendota and Wingra sediments contain greater N reserves held in an insoluble form which cannot be readily leached. Juday et al. (1941) have analyzed bottom deposits of 21 Wisconsin lakes for organic C and organic N, and the magnitude of C/N ratio appears to be independent of lake types. The C/N ratios of lake sediments found by Juday et al. (1941) range from 7.5 to 14.1. The average C/N ratio of agriculturally important surface soils is approximately 11 (Mortensen and Himes, 1964).

Exchangeable Ammonium Nitrogen. In Table 5.2 is shown the concentration range and mean concentration for exchangeable NH_4^+-N in the pre- and postcultural sediments of the four cores examined. The concentration of exchangeable NH_4^+-N generally increases with sediment depth for lakes Wingra, Monona and Trout, but decreases slightly for Mendota. The general increase in exchangeable NH_4^+-N with depth may indicate that organic materials are undergoing decomposition throughout most of the depth sampled. The NH_4^+-N released could be contained in the interstitial waters or incorporated in the adsorbing complex as exchangeable ammonium. Emery and Rittenberg (1952) observed from California Basin sediments that ammonia increased in the interstitial waters with sediment depth which was correlated with greater decomposition of organic matter with depth. The maximum rate of ammonia production is probably at or near the surface, but if oxidizing conditions exist in the surface layers, the nitrifying bacteria can convert the ammonia to nitrate. The low ammonia concentration observed in the upper layers is, then, the

Table 5.2 Exchangeable Ammonium Concentrations in the Pre- and Postcultural Sediments of Lakes Mendota, Monona, Wingra and Trout.

Lake	Precultural range NH_4^+-N (mg/g)	Precultural mean NH_4^+-N (mg/g)	Postcultural range NH_4^+-N (mg/g)	Postcultural mean NH_4^+-N (mg/g)
Mendota (WC-89)	0.34-0.49	0.41	0.41-0.54	0.49
Monona (WC-101)	---	---	0.20-0.96	0.74
Wingra	0.20-0.23	0.22	0.048-0.22	0.14
Trout, S. (WC-59)	0.24-0.34	0.29	0.16-0.26	0.22

difference between that oxidized by the nitrifying organisms and that formed in and brought into the layer from below. The increase in exchangeable NH_4^+-N with depth may also be due to the higher concentrations of organic N which can be mineralized residing at lower sediment depths. This may be especially true for lakes Wingra and Trout, since organic N generally increases with sediment depth. The correlation between organic N and exchangeable NH_4^+-N may best explain the rather uniform concentration of NH_4^+-N with depth of sediment for Mendota.

Keeney et al. (1970) reported 0.185, 0.127, 0.032 and 0.179 mg/g exchangeable ammonium N for the surface sediments of lakes Mendota, Monona, Wingra and Trout, respectively. All of these values with the exception of NH_4^+-N for Trout Lake are below the exchangeable NH_4^+-N content found in this study. In general, Keeney et al. (1970) found the soft-water sediments possessed greater amounts of exchangeable NH_4^+-N than hard-water lakes. This was attributed to the higher exchange capacity of the amorphous northern lake sediments. However, the higher exchangeable NH_4^+-N concentration of the northern lakes could also be attributed to the higher concentrations of original organic matter which can be mineralized.

Inorganic Nitrogen Released from Lake Mendota Sediments. The pre- and postcultural sediments of Mendota release increasing amounts of NO_3^-+ NH_3+NO_2^--N throughout the 50 day aerobic incubation period. As shown in Table 5.3 the release rate of inorganic N is 0.022 mg/l/day and 0.0098 mg/l/day for the pre- and postcultural sediments, respectively.Although both the pre- and postcultural sediments of Lake Mendota release inorganic N aerobically, the release rate of NO_2^-+NH_3+NO_3^--N on a mg/l/day basis is 2.2 times faster in the marl sediment, but the amount of inorganic N released per gram of sediment N is only 1.6 times greater in the marl than the gyttja. The hydrolyzable organic N released as NO_3^-+ NH_3+NO_2^--N for the gyttja and marl sediment at the end of the aeration period is 5.3 and 8.2 percent, respectively. This calculation assumes 80 percent of the total organic N is hydrolyzable (Keeney et al., 1970) and the organic C/organic N ratio is 8.55. The organic C concentration (organic N determined by mean C/N ratio from Mendota core WC-89) in the starting material for the two sediment types is approximately equal.

The initial inorganic N form produced by bacterial decomposition of organic material is ammonia. Under certain conditions, ammonia is converted to nitrite and then to nitrate by specific groups of bacteria. Austin (1970) found that nitrate N was the dominant inorganic form released from well-mixed aerobic incubation studies of Lake Mendota muds. After 170-200 days the ammonia concentration was practically reduced to zero (Austin, 1970). Austin (1970) reported higher values than this

Table 5.3 Inorganic Nitrogen ($NO_3^- + NH_3 + NO_2^- - N$) Released from Lake Mendota Pre- and Postcultural Sediments .

Sediment	Sed. in Suspension (g/1)	*Organic N in Sed. (mg/g)	Percent Hydrolyzable Organic N Released as $NO_3^- + NH_3 + NO_2^- - N$	Rates of Release of $NO_3^- + NH_3 + NO_2^- - N$		
				(mg N/1/da)	(mg N/g sed./da)	(mg N/g sed. N/da)
Post-cultural	3.29	10.1 (8.10)	5.30	0.0098 (2-58 da)	7.7×10^{-3}	9.5×10^{-1}
Pre-cultural	3.28	9.46 (7.55)	8.22	0.022 (1-53 da)	1.2×10^{-2}	1.55

* Numbers in parenthesis used in calculation of release rates; assumes 80 percent of organic N hydrolyzable N (see Keeney et al., 1970)

study for the rate of aerobic release of inorganic N (0.09 mg/l/day) and the percent of hydrolyzable N released as inorganic N (20.7 percent in 60 days) from Mendota gyttja. The conditions for the two studies were essentially the same; however, Austin used different analytical procedures for the determination of inorganic N forms. Mortimer (1941) noted a fall in alkalinity, nitrate and ammonia concentrations in an aerated artificial mud-water system. The laboratory conditions of Mortimer's studies were different than this or Austin's (1970) study. Mortimer allowed a surface brown "oxidized layer" to form on the muds before beginning the study and then kept the mud-water system quiescent, the temperature at 14-20°C and exposed to the light. The small change in dissolved substances in the aerated tanks was explained by Mortimer as due to the strongly adsorbent properties of the oxidized surface layers for bases such as ammonia. Sawyer (1944) also conducted an aerobic quiescent N release study on Mendota mud and found approximately 3.7×10^{-4} mg N/g sed/day (making assumption that solids content in 1 liter of mud from Sawyer's study was 20 percent). This is considerably less N release than found in this study. Sawyer does not comment on the N forms analyzed. In an aerobic N release study on uncultivated marsh soils (Shakey Marsh, Wis.), Bentley (1969) found a release of NO_3^--N of 0.0165 mg/l/day. This value is slightly greater than the release of inorganic N obtained for the Mendota postcultural sediment but slightly less than the precultural sediment.

It would appear historically the sediment potential for the aerobic release of inorganic N was similar to (or greater than) the postcultural period. Although the release rates of inorganic N shown in this study represent maximum release conditions, it seems that laboratory conditions might be correlated with mixed bottom muds from shallow bay areas in the summertime.

C. Distribution of Phosphorus

Total P analysis was performed on all cores investigated and acid soluble P was determined on Mendota cores WC-89 and WC-86, Wingra core WC-92, and Trout core WC-59. To discuss the factors believed to be controlling the deposition of P, a review of the various possible modes of P deposition in lakes is desirable. The migration and precipitation of P into the bottom muds may take place both by P incorporation into plant and animal remains and by sorption or precipitation with inorganic components. The final concentration of P residing in the sediment depends primarily on 1) the rates of supply of P in the form of inorganic and organic P from inflowing waters 2) the efficiency at which P is precipitated or sorbed with other chemical components such as Ca, Al, Fe and Mn or sorbed onto particulate matter and carried into the sediment, 3) the retentive capacity of the sediments for P and 4) the rate of accumulation of the whole sediment. Some insight is given as to the importance of these factors in the sedimentation of P in calcareous and noncalcareous lakes. The last factor mentioned will not be discussed explicitly because it is understood from the previous discussion of the role of this variable in the interpretation of a concentration-depth diagram.

Calcareous Lakes. In lakes Mendota and Monona the P concentration increases in the postcultural over the precultural sediment; in Wingra the mean P concentration of the pre- and postcultural sediments is approximately the same.

Any of the observed increases in the concentration of sorbed or precipitated P in the sediment could be attributed to an increase in the supply of P to the waters of a particular lake basin. The enrichment of P in the postcultural sediments of Mendota is of particular interest because the long core (9.9 m) provides a background concentration of P that was deposited for a long period historically. The interval from 990 to 62 cm presents the time prior to settlement period in southern Wisconsin. During this time the concentration of P, Fe, Mn, Al, K, Ca and ragweed pollen are all relatively constant indicating long stable conditions existed in Mendota and its watershed. It probably can be assumed that all four factors mentioned in controlling the distribution of P maintain a relatively constant ratio to each other during this period. The chemical homogeneity of the sediments is interrupted near the transition zone from high to low carbonates, whereby the components mentioned above are enriched in the postcultural sediments. Phosphorus increases in concentration by approximately 2-fold in the upper black gyttja. The sedimentation intensity of P is estimated at 11.9 mg P/cm^2/100 yr in the center of the lake. The estimated precultural P deposition rate is 1.5 to 2.2 mg P/cm^2/100 yr which is 5 to 8 times less than the postcultural deposition rate in the center of the lake. As a comparison, the postcultural sedimentation intensity of P for Monona and Wingra is 19.2 and 8.9 mg P/cm^2/100 yr, respectively. The deposition rate of P in Wingra sediments is low in spite of the high sedimentation rate in the Wingra basin. Wingra receives primarily urban runoff, but Mendota and Monona receive a combination of urban and agricultural runoff plus municipal sewage discharges. The accumulation rate of P in the sediments of Monona compare very well with that found by Ahlgren (1967) for

Lake Norrviken, a eutrophicated Swedish lake. From a water balance and P budget data, Ahlgren calculated a P deposition rate of 19.8 $mg/cm^2/100$ yr.

Another interacting variable controlling the final concentration of P in the sediments is the efficiency at which P is precipitated or sorbed with other chemical constituents. In lakes Mendota and Monona the P enrichment is concomitant with an increase in K, Fe, Mn and Al. These elements with exception of P are also enriched in the post-cultural sediments of Wingra. An increased influx of Fe and Mn hydrous oxides, clay minerals and oxides and hydroxides of Al from domestic drainage of urban and rural areas probably provides for increased efficiency for P precipitation. Phosphorus may be taken from solution by precipitated ferric and aluminum hydroxides or clay minerals (Carritt and Goodgal, 1954; Hsu, 1965). In general, high P sorption by clays is favored by a lower pH. A pH above 7 does not favor a strong fixation of P on clay minerals (Carritt and Goodall, 1954), but exchange reactions between P and mineral constituents might occur, or being accumulated on the surface, the P might move into the voids in the structure of solids (Carritt and Goodall, 1954). An eroded colloidal soil, low in P, might remove considerable amounts of P from the water before final deposition. Wang and Brabec (1969) have shown that the turbidity in Illinois River water was related to particulate P, particulate Si and particulate Fe (III). With the increase in runoff waters since the advent of agricultural practices in the Mendota watershed, a particulate P-Fe-Si complex associated with clay minerals similar to that proposed by Wang and Brabec may well have contributed to the P deposition increase since the cultural period. The mode of P deposition which is favored in the calcareous lake system is sorption or precipitation with $CaCO_3$ (Frink, 1969; Wentz and Lee, 1969b). At low concentrations of P (lake water), sorption on $CaCO_3$ is favored over precipitation (Cole et al., 1953). Also Al-P and Fe-P carried from the acidic watershed soils can be transformed to Ca-P upon residence in a neutral or basic lake environment (Frink, 1969). Wentz and Lee (1969b) found about one-half of total P is associated with the carbonate portion of the sediment in Lake Mendota. They concluded that the rate of increasing available (acid soluble) P deposition resulted from sorption onto clastic material or carbonate and that the above mechanism of P deposition required an increase in P concentration in the lake (Wentz and Lee, 1969b). This, they felt, was probably sustained by an increasing P influx due to urbanization. The acid soluble P extracted with 1 N HCl-H_2SO_4 on Mendota core WC-86 and Wingra WC-92 indicates the postcultural sediment contains the greater proportion of the total P which is not acid extractable. The strong acid treatment extracts Ca-bound P and non-occluded P. The non-occluded P includes P associated with Fe hydrous oxides and Al hydroxides and oxides precipitated or sorbed on the sediment particles, but 1 N acid probably would not extract organic P or occluded forms of Fe-P and Al-P (Shah et al., 1968). Thus, the more recent muds contain more P which is refractory or not readily exchangeable to the overlying water, whereas the marl sediments contain primarily Ca-bound P with a smaller proportion of the total P present as nonexchangeable P. Williams et al. (1970) reported values indicating that 26 percent of the total P is organic P in Mendota and Monona surface muds, and about 38 percent is organic P in Wingra surface sediments.

The final concentration of P that resides in the sediment is also dependent on the P sorptive and retentive capacity of the sediment. The aerobic sorption and desorption studies of P indicate the post-cultural gyttja is a more favorable sorptive and less favorable desorptive environment for P than the precultural marl in Lake Mendota. The higher concentration of Fe, Mn, Al, and K in the postcultural sediments than in the marl deposits probably accounts for the greater P binding capacity. Thus, it appears that for a long period historically the marl sediment was less capable of sorbing and retaining P, but in recent lake history the muds are more capable of sorbing and retaining P which may be added to the lake. If the P retentive capacity of the postcultural vs. the precultural muds were the sole influence in controlling P availability to aquatic plant growth, the lake would be in a phase of decreasing productivity. Livingstone and Boykin (1962) noted that the productivity in a lake could be inversely proportional to the sorptive capacity of the mud. They found the P content was highest in the deeper-lying samples of the sedimentary column of Linsley Pond, which formed during oligotrophic stage in the lakes history. In such a case, the P that had not been released from the mud during the early history of the lake would still be trapped in the sediment. The opposite trends that Livingstone and Boykin described take place in Lake Mendota. Presumably, the lake was less productive at the time of marl deposition, but the sorptive capacity and the P content is less in the marl sediment.

Wingra pre- and postcultural sediments sorb about 2-3 times less P than Mendota. In Wingra the sorption and desorption of P indicate the postcultural sediment is a less favorable sorptive and more favorable desorptive environment for P than the precultural sediment. Both of the above observations may partially account for low concentration of P in Wingra sediments compared to Mendota as well as the P profile for Wingra, which is rather uniform with depth. Since the P binding capacity in the Wingra postcultural sediments is low, the P accumulation is also low in the postcultural sediment. It appears that low Fe (8-9 mg/g) and high $CaCO_3$ (56-62 percent) content of the Wingra postcultural sediments accounts for the low P sorptive and high desorptive capacity, but apparently, the precultural marl containing a higher percentage of $CaCO_3$ (68-80 percent) enhances the sorption and reduces desorption of P. Nevertheless, the $CaCO_3$ and Fe content do not explain the sorptive-desorptive behavior of P completely, because the capacity of Wingra sediments for P sorption is much less than Mendota even though the marl sediment of Mendota and the top sediment of Wingra contain approximately the same concentrations of organic C, Fe, and $CaCO_3$. The difference in the Wingra postcultural and Mendota precultural sediment P sorptive-desorptive capacity may be due to physical characteristics as well, i.e. particle size differences. Any addition of P to Lake Wingra would be less capable of fixation by the recent muds than muds laid down preculturally.

Even though the sorptive-desorptive characteristics of Mendota postcultural muds favor an accumulation of P compared to the marl, the aerobic leaching studies on the pre- and postcultural Mendota sediments indicate a slightly greater release of P from the gyttja in an aerobic well-mixed system as shown in Table 5.4. The dissolved inorganic P released from Mendota pre- and postcultural sediments is 0.73 and 1.2 mg P/g sediment P/day, respectively. The P release data from this study agrees well with that of Spear (1970) who found that the surface sediment of Lake Mendota in an oxic system released 1.6 mg P/g sediment P/day (average) compared to 1.2 mg P/g sediment P/day observed in this study. The release rate of P based on a mg/l/day basis is about 3 times faster for the gyttja sediment, but the amount of P released per gram of sediment P is only 1.6 times greater in the gyttja than the marl. If the Lake Mendota muds became more reducing in the postcultural period as evidenced by the black coloration due to ferrous sulfides (Murray, 1956; Nriagu, 1967-68), the greater regeneration of P into the water phase may be expected under bottom anoxia conditions. Spear (1970) showed that about 5-12 times more P is released in Mendota surface sediments under anoxic (in 10 days) than oxic conditions (in 50 days). It is not known whether reducing conditions of the bottom muds would have an effect on the net loss of P from the sediments in a stratified lake on an annual basis.

The change in concentration and deposition rate of P in a horizontal direction in pre- and postcultural sediments from the deep-water area towards University Bay of Lake Mendota is depicted in Figure 5.1. The comparative values for deposition rate and concentration of P at the different core locations are calculated from a value of unity for the Mendota postcultural P concentration and deposition rate. The net effect of the cultural influence on the Mendota deep-water core profile

Table 5.4 Dissolved Inorganic Phosphorus Released from Lake Mendota Pre- and Postcultural Sediments.

Sediment	Sed. in Suspension (g/l)	P in Sed. (mg/g)	Percent Sed. P Released as Dissolved P	Rates of Release		
				(mg P/l/da.)	(mg P/g sed./da.)	(mg P/g sed. P/da.)
Postcultural	3.29	1.83	5.63	6.2×10^{-3}	2.2×10^{-3}	1.19
Precultural	3.28	0.91	3.04	2.2×10^{-3}	6.6×10^{-4}	0.73

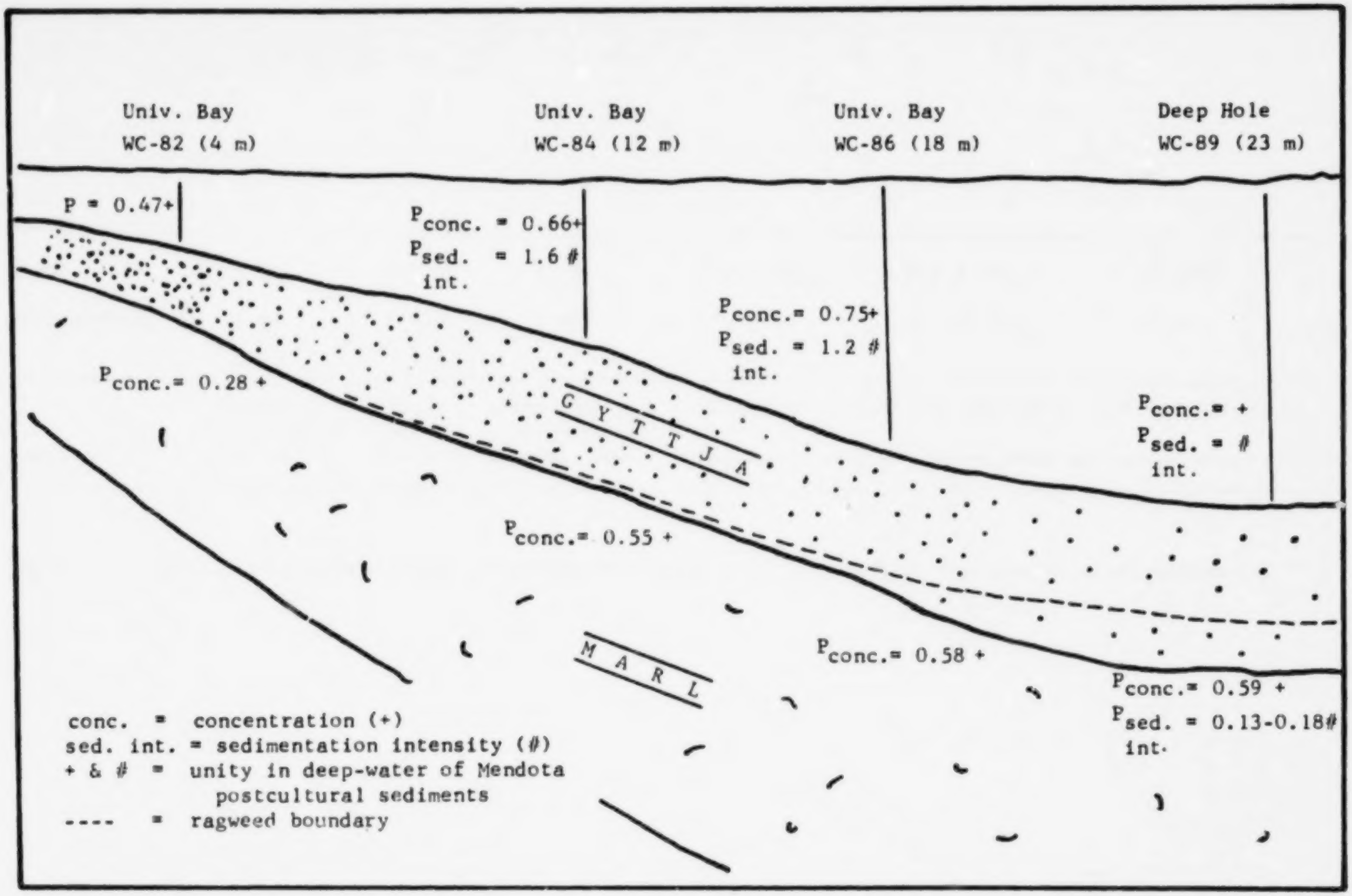

Univ. Bay
WC-82 (4 m)
Univ. Bay
WC-84 (12 m)
Univ. Bay
WC-86 (18 m)
Deep Hole
WC-89 (23 m)
P = 0.47+
$P_{conc.}$ = 0.66+
$P_{sed.}$ = 1.6 #
int.
$P_{conc.}$= 0.75+
$P_{sed.}$ = 1.2 #
int.
$P_{conc.}$= +
$P_{sed.}$ = #
int.
$P_{conc.}$= 0.28 +
GYTTJA
$P_{conc.}$= 0.55 +
MARL
$P_{conc.}$= 0.58 +
$P_{conc.}$= 0.59 +
$P_{sed.}$ = 0.13-0.18#
int.
conc. = concentration (+)
sed. int. = sedimentation intensity (#)
+ & # = unity in deep-water of Mendota postcultural sediments
---- = ragweed boundary

Figure 5.1 Phosphorus Concentration and Sedimentation Intensity in Gyttja and Marl Sediments of University Bay and the Deep-water Area of Lake Mendota.

is to produce a 2-fold change in P concentration in the gyttja sediment over the marl. The concentration of P in the marl is fairly uniform horizontally, but in the postcultural sediments the P concentration increases towards the center of the lake. The sedimentation of P in the center of the lake is probably associated with the finer sediment fraction. Based on surface sampling of 32 stations in Lake Mendota, P, Fe and Mn concentrations show a positive statistical correlation with sample depth (Delfino et al., 1969); a linear correlation coefficient of 0.82, 0.74 and 0.81 was found for P, Fe and Mn, respectively. Frink (1969) found in eutrophic Bantam Lake, Connecticut, that the center of the lake is enriched in clay, organic matter, and P when compared with the sediments around the edge. The Fe-P and Al-P fractions were always highest in the finer fractions towards the center of the lake, but Ca-P decreased with increasing water depth in Bantam Lake and was associated with the coarser fraction (Frink, 1969).

Nevertheless, the actual rate of P sedimentation increases toward the shallow water of University Bay where the deposition rate of the whole sediment increases as shown by the increasing depth of the ragweed boundary and the increasing dry solids accumulation. The depth of the wet sediment thickness of the black gyttja increases with water depth, but the sediments contain less dry solids (see Figure 4.1). Apparently, in the center of the lake the black gyttja was laid down prior to major cultural influence as shown by the depth of the ragweed profile.

Noncalcareous Lakes. The P profiles from a wide range of noncalcareous lakes indicate that concentration of P in the underlying older sediments is less in relation to the postcultural sediments in most of the cores examined (see Table 4.9). Nevertheless, in both West and South Bay of Little St. Germain the P concentration decreases in the upper postcultural deposits, and in the southwest bay of Minocqua and Weber the mean P concentration in the pre- and postcultural sediments remains unchanged. In eutrophic Minocqua and Little St. Germain lakes in which the P is not enriched in the upper sediment, the concentrations of Al, K, Mg and Ca increase in both the lakes usually by over 50 percent in the postcultural over the precultural sediment. Thus, it appears that rapid erosion due to the activities of man in the basin of these drainage lakes caused an increase in the rate of inorganic diluent resulting in a concomitant decrease in P concentration. As mentioned previously, the general increase in inorganic sedimentation in the northern Wisconsin region followed the period of deforestation. The high sedimentation intensity of 14.7 and 20.5 mg $P/cm^2/100$ yr in the southwest bay of Minocqua and West Bay of Little St. Germain, respectively, is further evidence that the supply rate or depositional efficiency of P in these two lakes has probably not decreased in recent times. These values for sedimentation intensity of P are the highest found for the noncalcareous lakes. As a comparison, the deposition rate of P mentioned above in the southwest bay of Minocqua and West Bay of Little St. Germain are in the same range as the deposition rate of P in Monona and University Bay of Mendota (14.0-19.2 mg $P/cm^2/100$ yr).

In nearly all the noncalcareous lakes examined, P, Fe and Mn concentration profiles are closely related both in the pre- and postcultural sediments. It must be assumed that a very important part is played by both Fe and Mn compounds, not only in precipitation of P to the sediment but also in its retention therein. Several investigators have emphasized the significance of Fe and its hydrous oxides to the precipitation and sorption of P (Mortimer, 1942; MacPherson et al., 1958; Jitts, 1959); fewer investigators have emphasized the role of Mn as a sorptive complex for P fixation (Mackereth, 1966). The Fe compounds undoubtedly play a more dominant role than Mn because the average lithospheric concentration is 50 mg/g Fe to 1 mg/g Mn (Rankama and Sahama, 1949). Morgan and Stumm (1964) discussed the transformations of Fe and Mn that are important to the geochemistry of lake waters. An oxidized low pH environment would favor the binding of P, and a reduced high pH environment would favor the release of P and colloidal stability of Fe and Mn compounds. Spear (1970) demonstrated that increasing the pH of the low pH Trout Lake sediments with $NaCO_3$ or $CaCO_3$ caused a significant increase in P released under oxic conditions. Mackereth (1966) attributed the maximum concentrations of P in Windermere and Esthwaite to the high efficiency of coprecipitation of P with Fe and Mn compounds. The results from this study on noncalcareous Wisconsin lakes would agree with Mackereth's observation Invariably high or low Fe and Mn concentrations in the core profiles are concomitant with high and low P. This is the case whether the sediments are of pre- or postcultural origin, so the mechanism does not appear to have changed with the modifying activity of man in the watershed. However, Mackereth (1966) observed that in oligotrophic Ennerdale the Fe and P profiles were separated, and he concluded that P deposition was not influenced by variations in Fe and Mn, but the precipitation of P was largely biological and constant. Only in oligotrophic Weber Lake are the Fe, Mn and P concentration profiles not related. This is the case whether the sediments are pre- and postcultural origin, so the artificial additions of fertilizers to Weber Lake have not affected the observation. The concentration of Fe and Mn in both Weber Lake pre- and postcultural sediment is the lowest found in the noncalcareous lakes examined. The Fe profile of Weber Lake parallels that of Al, K and Mg indicating that the Fe is probably associated primarily with clay minerals which would provide little opportunity for P precipitation with Fe. The close relationship between the sedimentation intensity of P, Fe and Mn in the postcultural sediments of the noncalcareous lakes is shown in Table 5.5. In West Bay of Little St. Germain, southwest bay of Minocqua and the North and South Trout show the highest postcultural sedimentation intensity for P, Fe and Mn; in Devils Lake and Weber Lake, Fe, Mn and P deposition rate is lowest. It is also noticed that a high P sedimentation intensity is not necessarily correlated to the productivity classification of a lake. For example, the P sedimentation intensity for North and South Trout Lake is high, but the lakes are oligotrophic-mesotrophic.

The final concentration of P which resides in the noncalcareous sediments is also dependent on the sorptive-desorptive capacity of the sediments for P. In Table 5.6 is shown the net P retentive capacity (after sorption and desorption steps) of the pre- and postcultural sediments compared to some chemical characteristics of the sediments. The lakes are arranged in the order of their decreasing P retentive capacity in the postcultural sediments. This order (with the exception of

Table 5.5 Relationship Between Phosphorus, Iron and Manganese Sedimentation Intensity in Noncalcareous Lakes.

Lake	Productivity Classification	Postcultural Sedimentation Intensity (mg/cm^2/100 yr)		
		P	Fe	Mn
Little St. Germain, W.	eutrophic	20.5	207	2.95
Minocqua, S.W.	eutrophic	14.7	118	3.20
Trout, S.	mesotrophic-oligotrophic	12.6	129	6.21
Trout, N.	mesotrophic-oligotrophic	11.6	106	4.75
Minocqua, N.W.	eutrophic	5.75	49.8	0.664
Little John	eutrophic-mesotrophic	5.59	80.0	1.23
Devils	mesotrophic-oligotrophic	4.06	83.4	0.900
Weber	oligotrophic	2.76	10.8	0.204

Table 5.6 Comparison of Phosphorus Retentive Capacity and Chemical Characteristics of Noncalcareous Pre- and Postcultural Sediments.

		* Net Added P Sorbed as % Total Added P for Initial P Level (µ P/g)of				Fe	Mn	Al	Ca	organic C	P
		500	1000	2500	5000	mg/g					
Little St. Germain, W.	a	100	100	100	98	108	1.39	13.2	0.43	126	11.1
	b	100	100	100	98	113	2.54	10.3	0.44	228	15.8
Little John	a	99	97	87	59	49.7	0.823	22.0	1.92	254	4.07
	b	38	29	16	9	11.7	0.305	24.7	1.77	287	1.14
Minocqua, S.W.	a	96	95	83	63	70.8	1.90	33.4	1.55	123	9.55
	b	90	75	57	47	53.5	1.55	10.5	1.06	153	9.19
Trout, S.	a	91	84	63	46	52.5	2.13	--	3.00	135	5.05
	b	88	80	58	44	58.4	2.50	--	3.36	166	6.01
Devils	a	80	61	40	20	37.1	0.454	90.3	2.50	73.2	2.39
	b	47	28	15	12	21.2	0.217	58.9	1.81	143	0.936

* After sorption and desorption

a Postcultural sediment

b Precultural sediment

Little John Lake) also concurs with that of decreasing Fe and P which have accumulated in the sediments. The laboratory experiments show the postcultural sediment of Little John has a higher potential for P sorption than would be predicted by the relatively low Fe and P content. The organic C content of Little John sediments is twice as high as the other lakes. Generally, the effect of organic anions is to repress P fixation (Swenson et al., 1949; Struthers and Seiling, 1950). The low P content of Little John sediments might be attributed to a low supply of P available for sorption since Little John is a spring-fed lake. In Little John, Devils and in the southwest bay of Minocqua the precultural sediments retain less P than the postcultural sediments. This is correlated with lower Fe and Mn content in the older sediments in each case. The Fe content of the sediment appears to be the dominant influence in the P sorptive capacity. For example, even though the Al content is higher than Fe in Devils Lake sediments, the P sorption is low corresponding to the low Fe content. The organic C content does not have a discernable effect on the P retentive capacity in the presence of high concentrations of Fe.

The generally high P retentive capacity of the noncalcareous lakes is probably due to the surface-reactive amorphous Al and Fe hydroxy-polymers which have a marked ability to retain inorganic P (Hsu, 1965). In common soils, because of the effect of pH, surface-reactive amorphous Al and Fe hydroxy-polymers dominate the process of P fixation. For example, in slightly acidic or neutral medium (pH 6-7) of dilute P solution (such as in sediments), amorphous Al (or Fe) compounds are stable and P is adsorbed on the surface (Hsu, 1965).

The oxic leaching studies by Spear (1970) also indicate the high Fe content of Trout sediments is responsible for the extremely low quantities of P in solution after an extended period of equilibration (ca. 900 hours) at approximately pH 5. The acid extraction (1N HCl-H_2SO_4) releases 70-99 percent of the total P (mean 90 percent) throughout South Trout core WC-59; the acid soluble P concentration follows the total P profile. Williams et al. (1970) reported values for the inorganic P for surface samples of several noncalcareous lakes. The percent inorganic P was as follows:

lake	station	percent inorganic P	
Trout	1	90.4	
Trout	2	85.0	
Minocqua	1	83.0	
Minocqua	2	91.1	
Little John	1	82.3	
Devils	1	71.8	(Williams et al., 1970).

Thus, the high percentage of inorganic P in the noncalcareous lakes is further evidence that the mechanism controlling the P deposition is largely nonbiological and is probably controlled to a large degree by the iron reactions both in the pre- and postcultural sediments. The acid soluble P profile in the South Trout core indicates no change in trend of primarily inorganic P deposition with depth of sediment. It would be interesting to know whether a high percentage of P in Weber Lake is organic P, since it is the only lake examined in which the Fe, Mn and P association is not closely related.

Since the noncalcareous sediments have a very high P retentive capacity, it is difficult to attribute an enrichment of P due solely to an increase in the supply of P. For example, if the postcultural sediments shown in Table 5.6 are arranged in the order of their decreasing Fe content, this order concurs exactly to decreasing amounts of P found in the sediments. Likewise, if the precultural sediments are arranged in the order of their decreasing retentive capacity, the Fe and P content in the sediments also decrease. However, the Fe/P ratio of the pre- and postcultural shown in Table 5.7 provides some insight into the importance of the P supply increase vs. the Fe supply increase. In North Trout, in the northwest bay of Minocqua, Little John and Devils both Fe and P increase in the postcultural sediments, and in these lakes the Fe/P ratio is larger in the precultural sediments. A low Fe/P ratio in the postcultural sediment and a high Fe/P ratio in the precultural sediment indicates the P deposition increases in a greater proportion than Fe since the onset of cultural activities in the basin. This would imply that the P supply has increased in the lake. The above hypothesis seems to correspond to what is known about the P supply to the northwest bay of Minocqua. During the period 1935-1964 the treated sewage from the town of Minocqua was discharged to the northwest bay of Minocqua causing an increase in supply of P to the lake. As predicted the Fe/P ratio decreases in the postcultural over the precultural sediment. If the Fe/P were high and low in the post- and precultural sediments, respectively, the implication may be that the sedimentary P increase is due to greater depositional efficiency with Fe-containing compounds, while the P supply remained relatively constant. In the drainage lakes, South and West Bay of Little St. Germain and in the southwest bay of Minocqua the Fe/P ratio of the postcultural sediment increases over precultural sediment,

Table 5.7 Iron to Phosphorus Ratio of the Noncalcareous Pre- and Postcultural Sediments.

Lake		$Fe_{/P}$	*K(Fe)	K(P)
Little St. Germain, W.	a	10.1	o	--
	b	6.83		
Little St. Germain, S.	a	8.05	++	-
	b	4.94		
Trout, N.	a	9.08	++	+++
	b	22.2		
Trout, S.	a	10.2	o	+
	b	12.1		
Minocqua, S.W.	a	8.00	++	o
	b	6.20		
Minocqua, N.W.	a	8.69	+	+++
	b	14.1		
Weber	a	3.89	o	o
	b	3.50		
Little John	a	14.3	++	+++
	b	21.6		
Devils	a	20.5	++	+++
	b	24.3		

a Postcultural sediments

b Precultural sediments

* K Mean Fe and Mn concentration of postcultural over precultural sediments (see Table 5.9 for explanation of notation)

thus, indicating the Fe supply in the recent sediments increases in a greater proportion than the P. In Weber Lake there is no change in Fe/P ratio with depth of sediments which indicates stable conditions of Fe and P supply.

D. Distribution of Iron and Manganese

Total Fe and Mn analyses were performed on all the cores investigated. The distribution of Fe and Mn in the sediments may depend primarily on 1) the supply rate of particulate and dissolved Fe and Mn 2) the migration of Fe and Mn as influenced by redox conditions and 3) rate of accumulation of the whole sediment.

Of particular interest in regard to the influence of redox conditions in controlling Fe and Mn concentration is Mackereth's (1966) interpretation of the Fe and Mn distribution in the postglacial sediments of English lakes. Mackereth (1966) noted since Mn is reduced and mobilized at a higher redox potential than Fe, the separation of Fe and Mn is considerable depending on the redox conditions. During a progression from oxidizing to reducing conditions in a lake, Mn loss from the sediments begins before Fe loss, and during the reverse process of a change from reducing to oxidizing conditions, Fe begins to accumulate in the sediment before Mn does. Thermodynamic data predict the Fe compounds that should be expected in a lake environment, such as Fe carbonate, sulfide, silicate and hydroxide, are uniformly less soluble than the corresponding Mn compounds, and that ferrous ion is more easily oxidized than manganous ion under naturally occurring pH-Eh conditions (Borchert, 1965; Krumbein and Garrels, 1952). Mackereth (1966) considers the reductive separation of Fe and Mn both in the drainage system and in the lakes. For instance, when the transport in the drainage system occurs by reduction to the mobile manganous and ferrous forms, considerable separation of the two elements may be expected, since the Mn is more easily reduced than Fe. Mackereth postulated in Windermere the enrichment of Mn with respect to

Fe in the sediments soon after the end of glaciation was brought about by the onset of reducing conditions in the soils of sufficient intensity to produce manganous ion but not intense enough to effect the large scale reduction of iron to ferrous ions. Thus, Mn was preferentially removed from the drainage soils and carried into solution to the oxidized lake waters where deposited. Mackereth then postulated that the position of the marked fall in Mn concentration in the early deposits of Esthwaite represented the time of the first formation of an anaerobic hypolimnion, since Mn is released from the sediments during thermal stratification and carried into the epilimnion at the overturn and thereby removed from the lake.

Calcareous Lakes. The Fe and Mn content generally increases by 2-4 fold in the postcultural sediments over the precultural sediments in all the calcareous lakes examined. The postcultural deposition rate of Fe increases from the deep-water area of Mendota towards University Bay and varies from 151-342 mg Fe/cm^2/100 yr. The sedimentation intensity of Fe for Monona is approximately the same as Mendota core WC-86, while Wingra has the lowest deposition rate of 127 mg Fe/cm^2/100 yr. The sedimentation intensity of Mn, however, is more or less the same for all three lakes ranging from 8.3-11.1 mg Mn/cm^2/100 yr.

In Table 5.8 is shown the Fe/Mn ratio for post- and precultural sediments in each lake. In all of the cores, with the exception of the Mendota core WC-89, the Fe/Mn ratio in the postcultural sediments is higher than the precultural sediment. The Fe/Mn ratio in Mendota core WC-89 probably did not fit the trend because Mn in the top 10 cm of the core was particularly enriched, which reduced the Fe/Mn ratio considerably.

Table 5.8 Mean Iron:Manganese Weight Ratio for the Pre- and Postcultural Sediments of Calcareous Lakes.

	Mendota WC-95	Mendota WC-89	Mendota WC-86	Mendota WC-84	Monona WC-46	Wingra WC-92
Water depth (m)	(24 m)	(23 m)	(18 m)	(12 m)	(16 m)	(4 m)
Mean Fe/Mn Ratio for the Postcultural Sediment	20.3	18.4	25.6	31.0	23.2	13.4
Mean Fe/Mn Ratio for the Precultural Sediment	17.2	21.7	17.8	18.5	16.8	7.6

However, the long Mendota core also taken in the deep water shows a higher Fe/Mn ratio in the postcultural sediment; the mean Fe/Mn ratio for the depth of the marl sediment (62-970 cm) is 17.2 which is close to the mean Fe/Mn ratio found in marl sediment of the short Mendota and Monona cores.

The general increase in Fe to Mn in the postcultural sediments of calcareous lakes may be explained as due either to an increase in the rate of Fe supply over Mn or to the greater loss of Mn than Fe from the reduced bottom muds. In reduced bicarbonate-rich solutions Mn^{++} shows a greater solubility than Fe^{++} (Borchert, 1965), so the separation of Fe and Mn could take place in proceeding from higher to lower oxidizing conditions. Since the advent of domestic drainage to the lakes, lower redox conditions of the bottom waters and muds presumably have developed. Thus, a greater net migration of Mn from the sediments results in an increase in the Fe/Mn ratio. The higher Fe/Mn ratio in the postcultural sediments could also be due to a higher supply rate of Fe to Mn.

It is noticed that Fe/Mn ratio also increases in the postcultural with respect to the precultural sediment of Wingra which does not stratify or develop reducing conditions. Therefore, the high Fe/Mn ratio in the postcultural sediment cannot be attributed to the variation in redox potential in Wingra, but instead to the increase in Fe with respect to Mn supply. Although lower redox conditions favoring the loss of Mn over Fe since the cultural period cannot be discounted in Mendota and Monona sediments, it would appear that an increase in Fe over Mn supply would be the dominant influence. The latter explanation is supported by the fact that the postcultural deposition rate of Mn varies only slightly between all the calcareous cores examined, whereas the Fe deposition rate varies considerably between the different cores.

The Fe/Mn ratio in both the pre- and postcultural sediment of Wingra is less than Monona and Mendota deposits. In lakes Monona and Mendota the precipitation and re-solution of Mn oxides, hydrated oxides or carbonates are also a function of the deoxygenated summer hypolimnetic waters, whereas in the well-oxygenated waters of Wingra the precipitation of Mn compounds may be more efficient on an annual basis. This may account for the enrichment of Mn relative to Fe in Wingra sediments. It has already been concluded that the variation in redox conditions is not the dominant influence in the separation of Fe and Mn during the cultural period, but it may be that lakes Mendota and Monona experienced oxygen deficiency before the cultural period enough to make a contrast to the well-oxygenated waters of Wingra. Nriagu (1968) suggested that prior to the change in sedimentation of Lake Mendota associated with human activity the lake had developed an oxygen deficiency intense enough to cause reduction of sulfates to sulfides but was able to maintain its basin free of black muds by the process of self-purification. Also Fruh et al. (1966) observed the rate of oxygen depletion in the hypolimnion of Mendota has not changed appreciably for the past half-century.

Nriagu (1967) proposed from his studies of Fe and S in Lake Mendota cores that the progressive upward enrichment of Fe in the sediments is due either to the diagenetic migration of Fe in the interstitial waters maintaining an upward diffusive flux or to increased efficiency of precipitation and retention of ferrous iron in the sediments as sulfides. Nriagu (1967) found a positive relationship between Fe and sulfide S in the cores. However, a feature shared by the gyttja and marl is that the Fe content is greater than should be required to hold all the sulfur as FeS (Nriagu, 1967). Several investigators (Lynn and Bonatti, 1965; Nussman, 1965) have attributed the relatively high content of Mn found in the tops of sediment cores to the ionic or molecular diffusion of Mn upward in pore water solution. The Mn dissolves upon burial in reduced sediments, then slowly migrates and accumulates in the oxidized upper strata (Lynn and Bonatti, 1965). Such migration of Mn could, therefore, cause an increase in the Fe/Mn ratio in the top layers. There is a sharp upward enrichment of Mn evidenced by the low Fe/Mn ratio in the top 10 cm of deep-water Mendota core WC-89; however, the Mn is not enriched in the top 0-10 cm of any other calcareous cores investigated. Thus, it appears that the upward migration of Mn does not exert an overall influence causing the increase in Mn concentration in the uppermost layers of the postcultural sediments.

The increase in Fe supply is probably associated with increased runoff from the land. Wang and Brabec (1969) found the turbidity in Illinois river water, to be related to the particulate P, Si and Fe (III) concentrations. The molar ratio of Si to Fe (III) was 1:1.47. Carroll (1958) found the association of Fe with clay minerals is an important means whereby Fe is transported by rivers to lakes. According to Carroll, Fe is associated with clay minerals 1) as an essential constituent, 2) as a minor constituent within the crystal lattice and 3) as iron oxide on the surface of mineral platelets. The close relationships between the Fe, K and Al profiles in the calcareous lakes are further evidence that Fe is mainly associated with the clay mineral fraction. Analyses of the clay fractions of soils show that Fe is mainly associated with the finest fractions (the clay and silt grades), which have extremely large surface area (Carroll, 1958). This may account for the high concentrations of Fe found in the center of Lake Mendota.

Noncalcareous Lakes. In six of the nine noncalcareous lake cores examined in this study, the mean Fe concentration increases in the postcultural sediments over the precultural sediments; however, in West Bay of Little St. Germain, South Trout and Weber the mean Fe concentration in the pre- and postcultural sediments remains unchanged. The postcultural sedimentation rate varies from 10.8 to 207 mg/cm^2/100 yr for Fe and from 0.20 to 6.1 mg/cm^2/100 yr for Mn (see Table 5.5). The highest deposition rate for Mn was observed in Trout Lake. The high deposition rate of Fe is usually accompanied by a high deposition rate for Mn. Even though the concentrations of Fe and Mn in the noncalcareous lakes are higher than the calcareous lakes, the deposition rates of both Fe and Mn are higher in the calcareous lakes (i.e. 151-342 mg Fe/cm^2/100 yr and 8.3-11.1 mg Mn/cm^2/100 yr).

In Table 5.9 is shown the Fe/Mn ratio for the pre- and postcultural sediments in each lake. There are no uniform conditions for all the lakes of increasing or decreasing Fe/Mn ratio in the postcultural over the precultural sediments. Only in lakes Little St. Germain and Weber is the Fe/Mn ratio higher in the postcultural over the precultural sediment. In lakes Little John, North and South Trout and Devils, the Fe/Mn ratio is higher in the precultural sediment, and in the northwest and southwest bay of Minocqua, Devils and South Trout, the Fe/Mn remains unchanged in the pre- and postcultural sediments. Apparently, the Fe/Mn ratio does not indicate a change in redox conditions for the deep stratified lakes which would favor a loss in Mn with respect to Fe as might be expected if the bottom lake waters and muds are becoming more reducing. Only in Little St. Germain Lake where the Fe/Mn ratio is higher in the postcultural sediments is the selective migration of Mn out of the sediments under reduced lake conditions a plausible explanation. The high to low Fe/Mn ratio in the pre- and postcultural sediments, respectively, for North Trout and Little John, could be explained by changing redox conditions in the watershed soils. If the land supported lush vegetation in the precultural era, so that the Eh and pH of stream and groundwater would be low, the reductive efficiency would lead to increased migration and supply of Fe but little change in the rate of supply of Mn. The increase rate of Fe supply would increase the Fe/Mn ratio in the sediments. If the watershed soils after deforestation

Table 5.9 Mean Iron:Manganese Weight Ratio for the Pre- and Postcultural Sediments of Noncalcareous Lakes.

	Little St. Germain,W.	Little St. Germain,S.	Trout, N.	Trout, S.	Little John	Weber	Minocqua, N.W.	Minocqua, S.W.	Devils
Water depth (m)	(16 m)	(7 m)	(26 m)	(33 m)	(5 m)	(13 m)	(11 m)	(14 m)	(13 m)
Mean Fe/Mn ratio for postcultural sediment	70.6	117	23.3	21.0	66.6	52.6	76.4	37.3	93.7
Mean Fe/Mn ratio for precultural sediment	46.1	87.1	32.6	23.1	78.3	39.9	80.9	34.3	101
* $\underline{K}$	+++	++	--	o	--	++	o	o	o

$$* \ \underline{K} = \frac{\text{mean Fe/Mn ratio of postcultural sediment}}{\text{mean Fe/Mn ratio of precultural sediment}}$$

Notation: $1.1 > K \geq 0.9 = 0$ $1.1 < \underline{K} \leq 1.2 = +$ $0.9 > \underline{K} \geq 0.8 = -$

$1.2 < \underline{K} \leq 1.5 = ++$ $0.8 > \underline{K} \geq 0.5 = --$

$\underline{K} > 1.5 = +++$ $\underline{K} < 0.5 = ---$

became more oxidizing, the Fe would become less mobile in the drainage waters producing a low Fe/Mn ratio in sediments. In both of the above cases it is assumed the stream and groundwater drain constantly into oxidizing lake basins. If the Fe/Mn ratio remains unchanged, as in four noncalcareous cores examined, this is probably an indication that a variation in redox conditions in the soils or lake water is not a primary influence. A constant Fe/Mn ratio with depth of sediment may indicate as Mackereth (1966) has shown for Ennerdale, that the rate of transport of Fe and Mn is influenced mainly by erosional conditions which would not be expected to bring about a separation of the two elements.

In summary, it would appear that a variation in redox conditions in the lake basin or soils may account for the recent changes observed in the Fe/Mn ratio in Little St. Germain, Little John and North Trout, but in the other lakes examined there was no change in the Fe/Mn ratio with depth of sediment. However, in the lakes (with exception of South Trout) in which there was no change in the Fe/Mn ratio with depth of sediment, the Fe and Mn concentrations increase in the postcultural sediments. The general upward increase in Fe and Mn in most of the noncalcareous cores may possibly be brought about by an increase in the supply of soluble and particulate Fe and Mn from the ash of forest fires or by the exposure and leaching of the B horizon of the podzolic soils of the cutover or burned forests. The period of maximum disturbance from cutover forest occurred several decades ago (Curtis, 1959); therefore, other explanations are probably needed to account for the increase in Fe into the most recent upper layers of sediment. The changes in

Fe (and P) profiles of South Trout Lake are quite abrupt and fluctuating even though K, Mg and Ca concentration remains more or less constant in both the pre- and postcultural sediments. Thus, it seems the Fe supply to South Trout Lake is subject to fairly rapid changes in differential leaching and erosion from the outwash and till surrounding Trout Lake. The changes in sedimentary concentrations of Fe, Mn, P and organic C are more pronounced in three noncalcareous lakes examined (Little John, North Trout, and in the northwest bay of Minocqua) than changes in concentrations of Mg, Al, K and Ca-containing compounds during (and after) the deforestation period in northern Wisconsin.

E. Distribution of Aluminum, Potassium Magnesium and Calcium

Total Al, K, Ca and Mg analyses were performed on all the cores investigated. The distribution of these elements may depend primarily on 1) the rate of supply of dissolved and particulate mineral matter 2) the biological or chemical precipitation of carbonates and 3) the variation in the accumulation of the whole sediment. Aluminum, Mg, Ca and K may occur in a large variety of mineral structures such as feldspars, clay minerals and amorphous aluminosilicate gels. Mackereth (1966) noted that Na, K and Mg were associated with the mineral fraction of the sediment of English lakes, but Ca was not so clearly associated with mineral erosion. Calcium was evidently more easily leached from the soil than Mg. According to Mackereth, the Ca is abundantly predeposited into the English lake sediments only at times of very intense erosion when the rate of precipitation of clastic material is high enough to prevent removal by leaching of much Ca. In the noncalcareous Wisconsin lakes the Al, Mg, Ca and K profiles show a close relationship. There should, on the grounds discussed above, exist a direct relationship between Al, K, Mg and Ca content in the sediments and erosion intensity of the drainage basin of the noncalcareous lakes. In Table 5.10, the sedimentation intensity of Al is arranged in decreasing order for the northern Wisconsin noncalcareous lakes. The Mg and K deposition rates almost exactly concur to the order shown for Al, but the Ca deposition rate deviates somewhat from the order shown by Al, K and Mg. The postcultural deposition rate of K increases from the deep-water area of Mendota towards University Bay and varies from

Table 5.10 Sedimentation Intensity of Aluminum, Magnesium, Potassium and Calcium in Noncalcareous Lakes in Northern Wisconsin

Lake	Al	K	Mg	Ca
		mg/cm^2/100 yr		
Minocqua, S.W.	71.5	13.2	6.70	3.62
Trout, N.	52.4	9.20	6.55	4.83
Little John	39.2	8.65	6.60	4.52
Little St. Germain, W.	34.8	8.21	5.67	1.46
Minocqua, N.W.	28.6	8.36	3.50	2.31
Weber	26.2	6.00	2.22	0.575

72 to 189 mg K/cm^2/100 yr. The sedimentation intensity of K is 107 and 83 mg K/cm^2/100 yr in Monona and Wingra, respectively. In the southern calcareous lakes, the K and Al concentration is enriched by 2-5 times in the postcultural over the precultural sediments. The magnitude of the erosional activity since man has moved into the Madison lake region has been quite intense compared to most noncalcareous lakes in northern Wisconsin. The Ca (and Mg as dolomite) concentration in Mendota, Monona and Wingra sediments is dominated by the carbonate deposition and will not be discussed further here (see section on carbon distribution).

Noncalcareous Lakes. The area surrounding the northern lakes is covered with second-growth coniferous and deciduous vegetation indicating that fires or cutover forest have modified the ecology at one time, but the area has since recovered from the period of maximum disturbance from logging activity. Little St. Germain and the southwest bay of Minocqua (both drainage lakes) were the only lakes examined in this study in which Mg, Al, K and Ca-containing compounds increase in the postcultural over the precultural sediment. The increase of Mg, Al, K and Ca-containing compounds is correlated to the increased runoff and leaching of the soils during the deforestation period. The core profiles indicate that runoff of erosional products reached a peak approximately 40-80 years ago. The decline in erosional products after this period is attributed to the regrowth of vegetation and timber. Bormann et al. (1968) found the drainage water from a cutover forest showed net losses of Ca, Mg, Na and K which were 9, 8, 3 and 20 times greater, respectively, than similar losses from five undisturbed forest ecosystems.

Mackereth (1966) regarded the potential internal productivity of a lake basin to be determined in part by erosion rate characteristics in the drainage area. He maintained that in a regime of less intense erosion the soil in the drainage area accumulates and is held in a suitable spatial position to allow leaching of various nutrient elements into solution in a form which is available to the living populations of the lake, whereas in a drainage area of intense erosion, the soil is removed from the site of leaching and deposited in the sediment where it is effectively protected from leaching. Thus, according to Mackereth, periods of more intense erosion would then be unfavorable to high internal productivity in the lake, while periods of lower erosion intensity would favor higher internal productivity. If the sedimentation rate has generally increased in the postcultural period of the northern Wisconsin noncalcareous lakes, then according to Mackereth's view, the internal productivity of these lakes is not favored in recent times. The high sedimentation intensity of Al and K, as shown in Table 5.10, in oligotrophic-mesotrophic North Trout would tend to support Mackereth's contention. On the other hand, the low sedimentation intensity of Al and K of Weber Lake does not support this view. Nevertheless, the detection of changes in erosion rates may be useful information to evaluate the history of a lake. For instance, Cowgill and Hutchinson (1964) reported the whole biological association was altered in Lago di Monterosi near Rome at about 200 B.C. during a period of increased erosion in the watershed. Cultural eutrophication was initiated not by artificial liberation of specific nutrient elements into the water, but by a rather subtle change in hydrographic regime.

In Devils Lake the Mg, Al, K and Ca-containing compounds increase in the postcultural over the precultural sediments. The shoreline area of Devils Lake has been modified by the development of recreational areas, cottages and a railroad bed which probably accelerated the erosional activity in the region. Twenhofel and McKelvey (1939) thought the sources of sediment of greatest importance were not the quartzite cliffs and talus near Devils Lake but rather the shore and shallow bottoms composed of sands, silts and clays originally brought into the region by the ice sheets. They also thought the two streams entering Devils Lake were not contributing very large quantities of sediments, particularly of clastic character. The postcultural sedimentation intensity of Mg, Al, K-containing compounds is faster in Devils Lake than any of the northern noncalcareous lakes.

CHAPTER VI

EVALUATION OF THE RELATIONSHIP BETWEEN THE CHEMICAL COMPOSITION OF LAKE SEDIMENT CORES AND LAKE EUTROPHICATION
AND
SUGGESTIONS FOR FURTHER RESEARCH

The purpose of this chapter is to discuss, based on the experience gained from this study, the limitations and potentialities of using lake sediment cores to describe eutrophication, to offer suggestions for further research and to propose broad guidelines for other investigators to follow in pursuing a similar project.

A. Potentialities and Limitations of Using Lake Sediment Cores to Evaluate Eutrophication of Lakes.

Attention has been directed in this study to examining the recent changes in lake history through chemical analyses and interpretation of lake sediment cores. A lake is responsive to changes in its watershed, whether these occur slowly by natural means or at an accelerated rate through the intervention of man. The information needed to trace changing limnological and watershed conditions of a lake must come from a geologic record preserved in the lake sediments. The findings from this study have indicated that changes in the chemical stratigraphy of lake sediment cores can be traced to cultural activities in the watershed; these stratigraphic changes are especially pronounced in the southern calcareous lakes.

Limitations in Using Lake Sediment Cores to Describe Eutrophication. The limitations and logical complexities facing a paleolimnolist in attempting to describe past events of nature cannot be overlooked. This is due largely to the relative lack of control over what can be observed and the range in space and time the observed variables occupy. Nevertheless, a greater understanding of the changes from the past into the present is needed to yield insight into the effects that man's exploding activities have had on lakes. The change in sedimentation of Lake Mendota will be used to illustrate the constraints imposed in attempting to reconstruct lake history. The estimated deposition rate of P and organic C in the center of Lake Mendota is 5-8 and 3-5 times greater, respectively, in the postcultural sediment over the precultural sediment. However, if the same comparison was made in University Bay these estimates would change to account for the higher deposition rate of P and organic C at the University Bay location. Likewise, if core samples were taken throughout the Mendota basin, the concentration, the moisture content, density and sedimentation rate would vary; this would be especially true in a drainage lake such as Mendota where the tributaries of Yahara River, Six Mile Creek and Pheasant Branch Creek carry runoff from urban and rural lands. Based on the core sampling of University Bay and the deep-area of Mendota, it appears that the P concentration in the marl sediment is more uniform over the lake, but since the advent of domestic drainage the influent materials have allowed fractionation of sediment particles with water depth which has complicated the sedimentation regime of the postcultural sediments. In the northern noncalcareous lakes similarities as well as differences exist in the chemical stratigraphy of cores taken from separate bays within the same lake. Thus, the sampling complexities impose a limitation on making representative estimates of rate changes based on one or a few cores taken within a lake. This does not, however, restrict the investigator from using a specified location in lake as a reference point to compare recent and past sedimentation changes. The sampling dependency is then assumed to be a recognizable feature of the system. Limitations are thus placed on using chemical criteria of trophic status in a quantitative expression that is representative of the entire basin. In this study the center of the lake was chosen as a reference point to document changes that have occurred in recent vs. past times. The sampling dependency may vary considerably from lake to lake; drainage lakes situated in an agricultural region may represent the extreme in sampling dependency. It would be advantageous for future investigators working on these same lakes to use the same reference point. Further research should be directed into establishing the extent to which lake morphology, hydrologic regimes and geomorphology affect the reliability of using one or more cores to represent processes occurring in the entire basin.

If the deposition rate of P and organic C increases by several fold in the postcultural over the precultural Mendota sediments, the observed rate change may be accounted for by several processes acting to produce a combined effect. For instance, it appears that the enrichment of P in the postcultural sediments of Mendota and Monona is due not only to the increase in supply of P from domestic drainage, but to the increase in P retentive capacity of the postcultural sediment and to an increase of P deposition due to the concomitant increase in Fe, Mn and Al-containing compounds. The increase in organic C deposition rate in Lake Mendota represents both an increase in auto- and allochthonous organic C. An increase in a lake's own total production of organic C becomes mixed with and is indistinguishable from that of external origin. This again illustrates the fact that the link between changes in sedimentary chemistry and eutrophication is largely a qualitative expression. However, the conditions of nutrient and organic supply and their resultant deposition within a lake are of paramount importance, so lake sediment cores which are dated can be used to express the amounts of materials deposited to the lake bottom per unit time as a combined effect of several operating processes.

A difficulty in interpreting the response of lakes to man's influence is that the time span involved is short; the thickness of the sediments produced during postcultural interval is often less than 0.5 m of unconsolidated sediment. In two of the noncalcareous lakes examined in this study the depth of the postcultural column was only 15 cm thickness. The short time span ($<$ 150 years B.P.) involved does not allow C-14 measurements to be made with accuracy (see literature review); therefore, other means such as ragweed pollen analyses must be used to identify the base of the cultural horizon and to establish sedimentation rates. This method does not allow the establishment of series of dates within the postcultural interval (absolute time scale). An absolute time scale for postcultural lake sediments has never been constructed, to the author's knowledge, except by indirect methods. The concentration-depth diagrams are not completely satisfactory because of the constraint imposed by the method; the composition of sediment related to volume or weight does not take into account varying rates of sedimentation. Ideally the composition of sediments should be expressed both as concentration and as sedimentation intensity. Research should be directed toward estimating sedimentation rates for both pre- and post-cultural sediments of the calcareous and noncalcareous lakes in Wisconsin. To date there has not been a single well-dated core from any Wisconsin lake. It is the author's opinion that this aspect of limnology of Wisconsin lakes has been grossly neglected. Any dating accomplished from the lakes (and core locations) examined in this study would augment the data already produced.

The depth of sediment mixing will determine the resolution of the chemical stratigraphy. In other words, does the chemical record show changes of 5 years, 20 years or 50 years for a given interval size? If the sediment record is obscured by the mixing of old and new deposits, any rate expression derived to describe cultural eutrophication becomes less accurate. The results from this study indicate greater resolution is achieved in following sedimentary changes for P in Lake Mendota by fractionating a core into 2 cm rather than 5 cm intervals. If mixing were deeper than only the upper layers (ca. 2-5 cm) in Lake Mendota deep-water sediments, greater resolution would not be observed by taking 2 cm intervals. In Weber Lake the changes in chemical stratigraphy were quite pronounced in spite of the slow sedimentation rate. In order for the pronounced peaks to persist, the depth of the sediment mixing column must be short in Weber Lake. The evidence for the extent of mixing in lake sediments is quite conflicting. Undoubtedly, the depth of mixing of sediments would vary from lake to lake and locations within a lake.

In the interpretation of the sedimentary record the assumption is generally made that there has been essentially no movement of materials upward or downward except in the biologically active layer near the surface. Replicate cores taken from the center of Lake Mendota indicate the maximum P peak about 20 cm below the sediment-water interface can be reproduced. Thus, the extent of mixing does not appear to laterally or vertically change the overall distribution pattern of P in the deep-water area of Lake Mendota. Research needs to be directed at determining the depth at which new and old deposits are mixed below the sediment-water interface under various conditions and lake bottom types.

Finally, the primary materials that accumulate in the upper layers of a sediment core can be altered by postdepositional changes brought about by biological and chemical processes. The findings from this study indicate that organic C once deposited in historical sediment layers appears to resist further decomposition. In the Lake Mendota long core organic C concentration remains constant within a range of 59-77 mg/g organic C over the core interval of 62-900 cm. Decomposition of N-containing compounds with sediment depth is indicated by the C/N ratio in the South Trout Lake core. Sustained study needs to be given to the chemical transformations that occur in the recent unconsolidated sediments.

Potentialities of Using the Chemical Composition of Lake Sediment Cores to Describe Eutrophication. The composition of the sediments with depth and, therefore, with time presents a pattern of change which documents the progressive increment of materials deposited to the lake bottom. In most of the cores examined in this study, pronounced chemical changes occur contemporaneously with the break in the ragweed pollen profile. Thus, changes in the chemical stratigraphy can be traced to man's activities in the watershed. If it is assumed that the sedimentation rate throughout the period represented by the concentration-depth diagram is constant, a calculation can be made showing the incremental increase or decrease in concentration per unit thickness of sediment (or per year if time is estimated). However, this study has revealed that concentration-depth diagrams do not generally contain sufficient information to estimate an incremental rate change in nutrient concentration which accurately reflects changes in nutrient supply due to man's activities in the watershed. The deposition rate of the whole sediment imposes a constraint on the system which necessitates an absolute time scale in the pre- and postcultural sediments. This thesis is in good agreement with Mackereth's (1966) observation on English Lakes in which he states, "The observed changes in composition of the sediment can most easily be explained if the sediment is regarded as a sequence of soils derived from the drainage areas of the lakes. The composition of the residue eventually reaching the lake bed can then be accounted for in terms of the rate of erosion of the drainage basin rather than in terms of changing rates of organic productivity either on the drainage basin or in the lake waters." In effect, the concentration profiles for organic C and other nutrient components are diluted by allochthonous materials. This, in itself, is useful information because in such a situation the sedimentation rate is usually fast and the concentrations of nutrient material in the enclosing sediment may be less, which in turn may affect the dynamics of nutrient release rates from sediments. Nevertheless, if it can be shown by fact (or by deductive reasoning) that the sedimentation rate is constant throughout the interval in question, then the chemical data contained in the concentration-depth diagram conveys all the information about changes that is contained in the deposition rate diagram. For example, in Little John Lake and in the northwest bay of Minocqua the Al, K and Mg-containing compounds (associated with erosional products) do not increase in the postcultural sediments over the precultural sediments, so it will be assumed the sedimentation rate is constant (see Table 4.9). It was shown earlier from the Fe/P ratio in these lakes that the P supply has increased in the postcultural sediments (see Table 5.7). In Table 6.1 is shown a rate expression (i.e. percent P increase/yr) for P in the pre- and postcultural sediments of Little John and in the northwest bay of Minocqua. In both lakes the precultural sediment show a zero increase in P per year, but in the postcultural sediments the P increases at a rate of 1.3 and 1.1 mg/g P per year for the northwest bay of Minocqua and Little John, respectively. Although such a rate expression

Table 6.1 Average Percent Increase in Phosphorus Deposition in Little John and Northwest Bay of Minocqua.

Lake		Average Percent Increase of P (mg/g per 5 cm interval)	Average Percent Increase P (mg/g per year)
Minocqua, N.W.	a	42	1.3
	b	~ zero	~ zero
Little John	a	12	1.1
	b	~ zero	~ zero

a) Postcultural sediment
b) Precultural sediment

is informative, it may not be a justified derivation for all the lakes examined for the reasons stated above.

In this study the overall sedimentation rate of the postcultural column was used to transform the chemical data based on concentration to a deposition rate (see Table 4.12). This derivation then can be used to estimate a discrete rate change in nutrient concentration which can be related to eutrophication. For example, in the Lake Mendota long core the overall precultural deposition rate of P was estimated and compared to the postcultural interval. The P deposition rate increases 5-8 fold in the postcultural over the precultural interval in the center of Lake Mendota. A knowledge of chemical deposition rates provides insight into the overall understanding of eutrophication which cannot be revealed by a static measurement of concentration. For instance, the use of lake sediment cores elucidates the relationship between high concentrations of P in the sediments of the noncalcareous lakes and the low concentrations of P in the noncalcareous lakes. Even though the concentrations of P are much higher in the noncalcareous lakes, the deposition rate is usually about the same or less than in the calcareous lakes. Likewise, the mean concentration of P in the postcultural sediment of Lake Wingra is 3.1 times less than the deep-area of Lake Mendota, but the deposition rate of P in Wingra is only 1.3 times less than the deep-area of Lake Mendota. Eutrophication of a lake includes the accumulation of sediments. Such a process is evolutionary in nature and all lakes are affected to a greater or less extent by this phenomenon. The dry sediment accumulated in postcultural sediment column varies from 0.905 g/cm^2 to 2.42 g/cm^2 and from 7.15 to 17.2 g/cm^2 for the noncalcareous and calcareous lakes, respectively. The filling rate of Lake Wingra is about 9 times faster than Little John Lake; both of these lakes are shallow eutrophic lakes in their respective geological regions. Except for the lower dry sediment accumulation rates of Weber Lake and in the northwest bay of Minocqua Lake, the dry sediment accumulation is more or less uniform for the profundal postcultural sediments of the noncalcareous lakes.

The chemical composition of the sediment cores with depth and, therefore, with time presents a pattern of change in which the relationship between different elements can be elucidated in both the pre- and postcultural sediments. In all the noncalcareous lakes examined, P, Fe, and Mn concentration profiles are closely related. This is the case whether the sediments are pre- or postcultural origin, so the mechanism does not appear to have changed with the modifying activity of man in the watershed. In general, the aerobic sorption and desorption of P studies indicate the sediment laid down postculturally is a more favorable sorptive environment for P and a less favorable desorptive environment for P than sediment laid down prior to cultural influences. This is due primarily to the concurrent increase in Fe in the postcultural sediments for both calcareous and noncalcareous lakes. The generally high P retentive capacity of the noncalcareous lakes is probably due to the surface-reactive amorphous Al and Fe hydroxy-polymers. However, Fe rather than Al content appears to be the dominant influence in determining P retentive capacity of the pre- and postcultural sediments. The acid soluble P profile in the South Trout core indicates no change in trend of primarily inorganic P deposition with depth of sediment. The mechanism for controlling the P deposition is largely nonbiological and is probably controlled by the iron reactions both in the pre- and postcultural sediment. Oligotrophic Weber Lake was the only noncalcareous lake examined in which 1) the Fe profile was associated with Al, K and Mg-containing compounds and 2) the Fe, Mn and P profile were not associated to each other. As a comparison, in all the calcareous lakes the Fe and Mn profiles bear a relationship to the Al and K profiles indicating the Fe is probably associated primarily with the clay mineral fraction. The Fe/Mn ratio increases in the postcultural sediments over the precultural sediments of the calcareous lakes. The changes in Fe/Mn ratio are thought to be primarily the result of an increase in Fe relative to Mn supply in the postcultural sediment of Mendota and Monona.

Analysis of past rates of change must be taken together with the detection and measurement of recent man-induced changes. Therefore, the chemical stratigraphy of lake sediment cores provides the understanding which is needed to detect a change as an acceleration; only by detecting accelerations is it possible to distinguish between normal and cultural processes. For example, in Devils Lake the P concentration at 60 cm level (>400-600 years B.P.) begins to increase slowly from 1.0 mg/g to 1.24 mg/g; this change is followed by a rapid rise in P concentration from 1.24 mg/g to 2.39 mg/g in the postcultural interval. Even though Devils Lake is currently an oligotrophic-mesotrophic lake, the sediments reveal that a natural process has occurred which produced a slow change in the chemical composition of the sediment, and this was followed by man-induced changes in the watershed which have accelerated the process considerably. In North and South Trout, West Bay of Little St. Germain and in the northwest bay of Minocqua, Weber and Devils

Lake, the organic C shows a slight upward decrease before the postcultural period is initiated; this is followed by a rapid decline in organic C during the postcultural period. In the long Mendota core the "normal rate" of P change (before man's influence) with sediment depth is nearly zero. The chemical stratigraphy of the Lake Mendota core indicates that stable limnological and watershed conditions existed in the lake for a long period historically. The initial rise in P concentration begins at the 55-60 cm level (ca. 140-170 years B.P.) before the appearance of high ragweed pollen counts. At the 35-40 cm level corresponding to the break in the ragweed curve, the P concentration is accelerated. A slow upward increase in P concentration below the break in the ragweed curve is also observed for the Monona core. This trend is followed by a rapid upward increase in P, but the periodic high sources of P from the sewage effluent discharged to Monona do not seem to be reflected in the upper sedimentary P concentration profile. Apparently the P from these sources is masked by sources of P from urban and agricultural runoff. In Little John, Devils, North Trout and the northwest bay of Minocqua, the "normal rate" of P and Fe change is also nearly zero (or increases upward slightly); this is followed by an accelerated increase in P and Fe concentration in the postcultural sediments.

Little St. Germain and the southwest bay of Minocqua (both drainage lakes) were the only lakes examined in this study in which Mg, Al, K and Ca-containing compounds increase in the postcultural over the precultural sediment. The increase of Mg, Al, K and Ca-containing compounds is correlated to the increased runoff and leaching of the soils during the deforestation period. The core profiles indicate that the runoff of erosional products reached a peak approximately 40-80 years ago. The decline in erosional products after this period is attributed to the regrowth of vegetation and timber. In the other northern lakes studied, including Trout Lake which is a drainage lake, the evidence from the core profiles indicates that the changes in concentrations of Fe, Mn, P and organic C are more pronounced than changes in concentrations of Mg, Al, K and Ca-containing compounds during (and after) the deforestation period.

Lake sediment cores are a particularly useful tool in assessing how changes in the chemical composition or state of sediment may have affected the retention and release of nutrients historically in the lake. If the lake sediments are considered as a part of the dynamic trophic system, then it is worthwhile to consider not merely the reserve of nutrients in sediments, but also how the change in chemistry brought about by cultural activities has affected the potential for release or retention of nutrients. For instance, the leaching studies on the Lake Mendota marl and gyttja indicate that inorganic N release is favored in the marl over the gyttja sediments. The limnological implication would be that the potential existed for the oxic release of inorganic N in precultural sediments which is similar to (or greater than) the recent sediments. The retentive capacity of P has increased in the postcultural sediments of Mendota, but the aerobic release of P is slightly favored in the gyttja over the marl sediments. The release rate of P is about 3 times faster for the gyttja sediment, but the absolute amount of P released per gram sediment is only 1.6 times greater in the gyttja than the marl.

Finally, the chemical stratigraphy of lake sediment cores can serve as a record for future investigators to follow changes 20, 50 or 100 years from now. Since the overall chemistry has been performed on the cores from several lakes, future investigators can judiciously select intervals along a core column to perform analyses corresponding to certain changes.

B. Guidelines for Future Lake Sediment Coring Studies

Coring Location. The center of the lake is probably the most convenient reference point. The mixing of bottom sediments and the inflow of detrital materials from the shore regions may be minimal at the central location in a lake. Deep, closed basin lakes with flat bottom contour lines probably provide the best type of coring site--i.e. Devils Lake. In order to effectively evaluate changes in recent sediments of drainage lakes and lakes with multiple bay areas, more than a single core needs to be taken. Core traverses should be made in lakes whenever possible.

Coring Apparatus. A large diameter (3½ inches) piston-operated corer of 1 meter length provides for minimum disturbance of the core material, sufficient sample for chemical analyses and sufficient depth to penetrate the pre- and postcultural sediments. The reader should refer to Wentz (1967) and Bortleson (1968) for details of the coring apparatus used in this study.

Fractionation. The optimum interval size depends on the sedimentation rate and the depth of sediment mixing. The resolution expected in a sediment core can be estimated by making a preliminary analyses of a given component along the core column using smaller and smaller interval sizes until the smallest interval used shows no difference in the inflection of the profile peaks. In general, a 2-5 cm interval size should allow sufficient detail of the chemical stratigraphy of the post-cultural sediments. It is wise, however, to sample in as small intervals as practical. The investigator always has the option to use selected intervals and to combine sections at a later stage depending on the physical and chemical characteristics of the core and the amount of sample needed for analyses. The reader is referred to Davis (1967) for techniques in sampling cores at intervals as small as 4 mm. If long cores penetrating the depth of the postglacial column are taken, they should be at the same site as the shallow cores in order to directly compare the post- and precultural chemical composition and sedimentation rates. The fractionation of the long cores should be taken in relatively small intervals (10-20 cm).

Storage. The core samples should be stored in glass bottles at 4°C until the physical parameters such as percent moisture, bulk density grain specific gravity and wet chemical analyses are measured or performed. The investigator may consider freezing the samples for long-term storage after the above analyses are completed. If the investigator is determining various forms of an element which comprise a fraction of the total, special precaution must be taken to properly store the samples. For instance, the analysis of various forms of nitrogenous compounds may vary depending on the storage and handling of soil or sediment samples (Bremner, 1965). Since it is not often possible to predict changes upon storage, the best technique is to conduct tests to determine the analytical difference between storage under certain conditions vs. immediate analysis. The reader is referred to soils literature (Jackson, 1958) for information concerning the preservation of samples.

Chemical Analyses. The following chemical analyses may be of interest in evaluating the overall effects of eutrophication:

1) the biophile elements - C, N and P
2) elements influenced by redox conditions - Fe, Mn and S
3) Ca and Mg
4) elements associated with clay minerals - i.e. Al, Si and K
5) trace elements - i.e. Cu, As, Pb and Zn
6) extractable forms of cations, anions and nutrients
7) cation exchange capacity
8) pH and redox potential.

Dating Cores. Dating of recent sediments as discussed previously is problematic; however, more research should be directed into using tracers such as ragweed pollen, magnetic iron spherules, and man-introduced contaminants such as Cu, As and Pb. In addition, techniques such as Pb-210 dating and X-ray radiography need to be explored. The reader is referred to Kendall (1969), Davis (1967), Ogden (1967) for discussion on C-14 dating techniques. In order to arrive at a meaningful first approximation of sedimentation rates, a series of C-14 dates needs to be performed on a single core. It should be emphasized that dates are meaningless unless accompanied by physical data of sediment density and percent moisture.

Other Investigators. Paleolimnology as a whole is too vast a subject to be dealt with by one individual or with the view of one discipline.

It is recommended at the start of a coring program to involve other individuals. Although reports are not yet available, various investigators have obtained Lake Mendota core samples for pollen, ostracod, diatom, trace elements and Pb-210 dating. It is felt that the information that these investigators will obtain will provide additional insight into the use of the chemical composition of lake sediment cores to estimate the current degree and rate of eutrophication of lakes.

CHAPTER VII

SUMMARY

The chemical composition of 1 m sediment cores fractionated into 5 cm intervals was used to trace the recent developmental history of Lakes Mendota, Monona and Wingra (calcareous lakes in Dane Co., Wis.); Devils Lake (a noncalcareous lake in Sauk Co., Wis.); Little St. Germain Lake, Trout Lake, Lake Minocqua, Weber Lake and Little John Lake (noncalcareous lakes in Vilas and Oneida Co., Wis.). The sediment cores were analyzed for C, P, Ca, Mg, K, Al, Fe and Mn. Organic C and carbonate C were determined separately. Organic N, exchangeable ammonium and acid soluble P determinations were performed on selected sedimentary profiles. Ambrosia (ragweed) pollen was used to establish recent sedimentation rates and to identify pre- and postcultural sediment in the core column.

Changes in the chemical stratigraphy of lake sediment cores are traced to cultural activities in the watershed; these stratigraphic changes are especially pronounced in the southern calcareous lakes. The enrichment of P in the postcultural sediments of Lake Mendota is due not only to an increase in supply of P from domestic drainage, but to an increase in P retentive capacity of the postcultural sediment and to an increase of P deposition due to the concomitant increase in Fe, Mn, K and Al-containing compounds. The chemical stratigraphy of a 9.9 m Lake Mendota core provided evidence that a long period of stable conditions existed in the lake and watershed prior to the settlement period in southern Wisconsin; the concentrations of organic C, P, Fe, Mn, Al, K, Ca and ragweed pollen are all relatively constant over the interval 62 to 990 cm. In Lake Mendota the "normal rate" of P change (before man's influence) with sediment depth is nearly zero. At the 35-40 cm level corresponding to the break in the ragweed curve, the P concentration is accelerated upward to sediment-water interface. The estimated post-cultural deposition rate of P (11.9 mg P/cm^2/100 yr) in the center of Lake Mendota is 5-8 times greater than the precultural interval.

A trend which is common to all the northern Wisconsin noncalcareous lakes is an increase in organic C concentration with depth of sediment. In several of the lakes the organic C shows a slight upward decrease before the postcultural period is initiated; this is followed by a rapid decline in organic C during the postcultural period. The decrease in organic C is usually accompanied by an increase in P, Fe, Mn and/or Al, K, Mg, Ca-containing compounds. The postcultural period is usually marked by an increase in inorganic sedimentation rate. Changes in sedimentary concentrations of Fe, Mn, P and organic C are more pronounced in three noncalcareous lakes than changes in concentrations of Mg, Al, K and Ca-containing compounds during (and after) the deforestation period in northern Wisconsin. The P, Fe and Mn concentration profiles are closely related in both the pre- and postcultural deposits. The concentration of P in sediments is largely controlled by Fe and to a lesser extent Mn deposition. In general, the aerobic sorption and desorption of P studies indicate the sediment laid down postculturally is a more favorable sorptive environment for P and a less favorable desorptive environment for P than sediment laid down prior to cultural influences. This is due primarily to the concurrent increase in Fe in the postcultural sediments for both calcareous and noncalcareous lakes. The postcultural sedimentation rate P (and Fe) is highest for the eutrophic drainage lakes West Bay of Little St. Germain Lake and the southwest bay of Lake Minocqua (20.5 and 14.7 mg P/cm^2/100 yr, respectively) and lowest for the two oligotrophic lakes, Devils Lake and Weber Lake (2.76 and 4.06 mg P/cm^2/100 yr, respectively).

Only in the special case of rate constant sediment accumulation can a rate expression be derived to estimate accurately an incremental change in nutrients to the lake basin. The chemical stratigraphy of concentration-depth diagrams do, however, permit a qualitative evaluation of the extent lakes have been influenced by man's activities. The potentialities and limitations of using recent lake sediments to evaluate cultural eutrophication of lakes are discussed.

LITERATURE CITED

Ahlgren, I., "Limnological Studies of Lake Norrviken, a Eutrophicated Swedish Lake," Schweizer. Zeitschrift für Hydrologie 29, 53-90 (1967)

Allgeier, R.J., Hafford, B.C., Juday, C., "Oxidation-Reduction Potentials and pH of Lake Waters and of Lake Sediments," Trans. Wis. Acad. Sci. Arts Lett. 34, 115-133 (1941).

Allison, L.E., Moodie, C.D., "Carbonate," In C.A. Black, ed., Methods of Soil Analysis Part 2, Amer. Soc. Agronomy, Madison, Wis., 1367-1378 (1965).

Ambühl, H., "Die künstliche Belüftung des Pfäffikersees. Orientierung über die ersten Ergebnisse," Verbands-Bericht VSA Nr. 77/3 9s. (1962).

Andersen, S.T., Silicone Oil as a Mounting Medium for Pollen Grains, Geological Survey of Denmark, Series IV, 5-24 (1960).

Andrews, L.M., Threinen, C.W., Surface Water Resources of Oneida County, Wis. Conservation Dept., 284 p. (1966).

Armstrong, W., "The Relationship between Oxidation-Reduction Potentials and Oxygen-Diffusion Levels in Some Waterlogged Organic Soils," J. Soil Sci. 18, 27-34 (1967).

Arrhenius, G., "Carbon and Nitrogen in Subaquatic Sediments," Geochimica et Cosmochimica Acta 1, 15-21 (1950).

Austin, E.R., "The Release of Nitrogenous Compounds from Lake Sediments," M.S. Thesis, Water Chemistry, Univ. of Wis., 78 p. (1970).

Bailey, G.W., "Role of Soils and Sediment in Water Pollution Control," FWPCA, Southeast Water Laboratory, 90 p. (1968).

Beeton, A.M., "Eutrophication of the St. Lawrence Great Lakes," Limnol. & Oceanogr. 10, 240-254 (1965).

Beeton, A.M., "Indices of Great Lakes Eutrophication," Great Lakes Research Division, Publ. No. 15, Univ. of Mich., 1-8 (1966).

Bender, M.M., Personal Communication, Meteorology, Univ. of Wis. (1969).

Bentley, E.M., "The Effect of Marshes on Water Quality," Ph.D. Thesis, Water Chemistry, Univ. of Wis. (1969).

Berg, K., "Studies on the Bottom Animals of Estrom Lake," Ejnar Manksgaard, Copenhagen (1938).

Berger, W.H., Heath, G.R., "Vertical Mixing in Pelagic Sediments," J. Marine Res. 26, 134-143 (1968).

Berner, R.A., "Distribution and Diagenesis of Sulfur in some Sediments from the Gulf of California," Marine Geol. 1, 117-140 (1964).

Black, C.A., "Geomorphology of Devils Lake Area, Wis.," Trans. Wis. Acad. Sci. Arts & Lett. 56, 117-148 (1967-1968).

Black, C.S., "Chemical Analysis of Lake Deposits," Trans. Wis. Acad. Sci. Arts Lett. 24, 127-133 (1929).

Black, J.J., Andrews, L.M., Threinen, C.W., Surface Water Resources of Vilas County, Wis. Conservation Dept., 316 p. (1963).

Borchert, H., "Formation of Marine Sedimentary Iron Ores," In J.P. Riley and G. Skirrow, eds., Chemical Oceanography Vol. 2., Academic Press, London and New York, 159-201 (1965).

Bordovskiy, O.K., "Accumulation and Transformation of Organic Substances in Marine Sediments. Part 4." Marine Geol. 3, 83-114 (1965).

Bormann, F.H., Likens, G.E., Fisher, D.W., Pierce, R.S., "Nutrient Loss Accelerated by Clear-cutting of a Forest Ecosystem," Science 159, 882-884 (1968).

Bortleson, G.C., "Chemistry of Lake Sediment Cores," M.S. Thesis, Water Chemistry, Univ. of Wis., 165 p. (1968).

Bremner, J.M., "Inorganic Forms of Nitrogen," In C.A. Black, ed., Methods of Soil Analysis, Part 2, Amer. Soc. Agronomy, Madison, Wis., 1149-1318 (1965).

Brezonik, P.L., Morgan, W.H., Shannon, E.E., Putnam, H.D., "Eutrophication Factors in North Central Florida Lakes," Bulletin Series No. 134, Water Resources Research Center Publ. No. 5, Univ. of Florida, 101 p. (1969).

Brown, S.R., "Paleolimnological Evidence from Fossil Pigments," Mitt. Internat. Verein. Limnol. 17, 95-103 (1969).

Bryson, R.A., Suomi, V.E., "The Circulation of Lake Mendota," Trans. Amer. Geophys. Union 33, 707-712 (1952).

Butkevich, V.S., "The Bacterial Population of the Caspian Sea and the Sea of Azov," Mikrobiologiya 7, 9 (1938).

Carritt, D.E., Goodgal, S., "Sorption Reactions and some Ecological Implications," Deep-Sea Res. 1, 224-243 (1954).

Carroll, D., "Role of Clay Minerals in the Transportation of Iron," Geochimica et Cosmochimica Acta 14, 1-27 (1958).

Chang, S.C., Jackson, M.L., "Fractionation of Soil Phosphorus," Soil Sci. 84, 133-144 (1957).

Charlton, D.S., "The Ecological and Sedimentological History of a Lake in Northern Wisconsin," M.S. Thesis, Geology Dept., Univ. of Wis., 105 p. (1969).

Cole, C.V., Olsen, S.R., Scott, C.O., "The Nature of Phosphate Sorption by Calcium Carbonate," Soil Sci. Soc. Amer. Proc. 17, 352-356 (1953).

Cole, G.A., "Notes on the Vertical Distribution of Organisms in the Profundal Sediments of Douglas Lake, Michigan," Amer. Midl. Naturalist 49, 252-256 (1953).

Conger, P.S., "The Contribution of Diatoms to the Sediments of Crystal Lake, Vilas County, Wisconsin," Amer. J. Sci. 237, 324-340 (1939).

Cowgill, U.M., Hutchinson, G.E., "Cultural Eutrophication in Lago di Monterosi during Roman Antiquity," Verh. Internat. Verein. Limnol. 15, 644-645 (1964).

Curtis, J.T., The Vegetation of Wisconsin, The Univ. of Wisconsin Press, 657 p. (1959).

Cushing, E.J., "Late-Wisconsin Pollen Stratigraphy and the Glacial Sequence in Minnesota," In Quaternary Paleoecology, E.J. Cushing and H.E. Wright, Jr. eds., Yale Univ. Press, New Haven, 59-88 (1967).

Davis, C.C., "Evidence for the Eutrophication of Lake Erie from Phytoplankton Records," Limnol. & Oceanogr. 9, 275-283 (1964).

Davis, M.B., Deevey, E.S.Jr., "Pollen Accumulation Rates: Estimates from Late-Glacial Sediments of Rogers Lake," Science 145, 1293-1295 (1964).

Davis, M.B., "Pollen Accumulation Rates at Rogers Lake, Connecticut, During Late- and Postglacial Time," Rev. Palaeobotan. Palynol. 2, 219-230 (1967).

Davis, M.B., "Pollen Grains in Lake Sediment Redoposition Caused by Seasonal Water Circulation," Science 162, 796-799 (1968).

Davis, R.B., "Pollen Studies of Near-Surface Sediments in Marine Lakes," In Quaternary Paleoecology, E.J. Cashing and H.E. Wright, Jr., eds., Yale Univ. Press, New Haven, 143-173 (1967).

Delfino, J.J., "Aqueous Environmental Chemistry of Manganes," Ph.D. Thesis, Water Chemistry, Univ. of Wis., 365 p. (1968).

Delfino, J.J., Bortleson, G.C., Lee, G.F., "Distribution of Mn, Fe, P, Mg, K, Na, and Ca in Surface Sediment of Lake Mendota, Wisconsin," Environ. Sci. & Tech. 3, 1189-1192 (1969).

Delfino, J.J., Lee, G.F., "Chemistry of Manganese in Lake Mendota, Wisconsin," Environ. Sci. & Tech. 2, 1094-1100 (1968).

Deevey, E.S., "Studies on Connecticut Lake Sediments. III. The Biostratonomy of Linsley Pond. Part II.," Amer. J. Sci. 240, 313-324 (1942).

Deevey, E.S., "Cladoceran Polulations of Rogers Lake, Connecticut, During Late- and Postglacial Time," Mitt. Internat. Verein. Limnol. 17, 56-63 (1969).

Degens, E.T., "Diagenesis of Organic Matter," In G. Larsen and G.V. Chilingar, eds., Diagenesis of Sediments, Elsevier Publ. Co., New York, 343-390 (1967).

Edmondson, W.T., "Water Quality Management and Lake Eutrophication: The Lake Washington Case," In T.H. Campbell and R.O. Sylvester, ed., Water Resources Management and Public Policy, Univ. of Washington Press, Seattle, 139-178 (1968).

Edmondson, W.T., "Cultural Eutrophication with Special Reference to Lake Washington," Mitt. Internat. Verein. Limnol. 17, 19-32 (1969).

Edmondson, W.T., Anderson, G.C., Peterson, D.R., "Artificial Eutrophication of Lake Washington," Limnol. & Oceanogr. 1, 47-53 (1956).

Emery, K.O., Rittenberg, S.C., "Early Diagenesis of California Basin Sediments in Relation to Origin of Oil," Bull. Am. Assoc. Petrol. Geologists 36, 735-806 (1952).

Faegri, K., Iversen, J., Textbook of Modern Pollen Analysis, Copenhagen, Ejnor Munksguard, 168 p. (1950).

Federal Water Pollution Control Administration, "Fertilization and Algae in Lake Sebasticook, Maine," Rept. of the Tech. Advisory and Investigations Activities, R.A. Taft San. Eng. Center, Cincinnati, Ohio, 124 p. (1966).

Fogg, G.E., Belcher, J.H., "Pigments from the Bottom Deposits of an English Lake," New Phytologists 60, 129-142 (1961).

Frey, D.G., "The Ecological Significance of Cladoceran Remains in Lake Sediments," Ecology 41, 684-699 (1960).

Frey, D.G., "Wisconsin: The Birge-Juday Era," In D.G. Frey, ed., Limnology of North America, 34-54 (1963).

Frey, D.G., "Remains of Animals in Quaternary Lake and Bog Sediments and Their Interpretations" Arch. Hydrobiol. Beih. Ergebn. Limnol. 2, 1-114 (1964).

Frey, D.G., "The Rationale of Paleolimnology," Mitt. Internat. Verein. Limnol. 17, 7-18 (1969).

Frey, D.G., "Evidence for Eutrophication from Remains of Organisms in Sediments," Eutrophication, Proceedings of a Symposium, National Academy of Sciences, Washington D.C., 594-613 (1969).

Frink, C.R., "Nutrient Budget: Rational Analysis of Eutrophication in a Connecticut Lake," Environ. Sci. & Tech. 1, 425-428 (1967).

Frink, C.R., "Chemical and Mineralogical Characteristics of Eutrophic Lake Sediments," Soil Sci. Soc. Amer. Proc. 33, 369-372 (1969).

Fruh, E.G., Stewart, K.M., Lee, G.F., Rohlich, G.A., "Measurement of Eutrophication and Trends," J. Water Poll. Contr. Fed. 38, 1237-1258 (1966).

Gould, H.R., Budinger, T.F., "Control of Sedimentation and Bottom Configuration by Convection Currents, Lake Washington, Washington," J. of Mar. Res. 17, 183-198 (1958).

Goulden, C.E., "Interpretative Studies of Cladoceran Microfossils in Lake Sediments," Mitt. Internat. Verein. Limnol. 17, 43-55 (1969).

Goulden, C.E., "Progressive Changes in the Cladoceran and Midge Fauna during the Ontogeny of Esthwaite Water," Verh. Internat. Verein. Limnol. 15, 1000-1005 (1964).

Gorham, E., "Observations on the Formation and Breakdown of the Oxidized Microzone of the Mud Surface of the Lake," Limnol. & Oceanogr. 3, 291-298 (1958).

Gorham, E., "Chlorophyll Derivatives, Sulfur, and Carbon in Sediment Cores from Two English Lakes," Can. J. Botany 39, 333-338 (1961).

Griffiths, M., Perrott, P.S., Edmondson, W.T., "Oscillaxanthin in the Sediment of Lake Washington," Limnol. & Oceanogr. 14, 317-326 (1969).

Harmsworth, R.V., Whiteside, M.C., "Relation of Cladoceran Remains in Lake Sediments to Primary Productivity of Lakes," Ecology 49, 998-1000 (1968).

Harter, R.D., "Adsorption of Phosphorus by Lake Sediment," Soil Sci. Soc. Amer. Proc. 32, 514-518 (1968).

Hasler, A.D., "Cultural Eutrophication is Reversible," Bioscience 19, 425-431 (1969).

Hayes, F.R., Phillips, J.E., "Lake Water and Sediment IV. Radiophosphorus Equilibrium with Mud, Plants and Bacteria under Oxidized and Reduced Conditions," Limnol. & Oceanogr. 3, 459-475 (1958).

Hayes, F.R., Reid, B.L., Cameron, H.L., "Lake Water and Sediment. I. Oxidation-Reduction at the Mud-Water Interface," Limnol. & Oceanogr. 3, 308-317 (1958).

Henrici, A.T., McCoy, E., "The Distribution of Heterotrophic Bacteria in the Bottom Deposits of Some Lakes," Trans. Wis. Acad. Sci. Arts Lett. 31, 323-361 (1938).

Holden, A.V., "The Removal of Dissolved Phosphate from Lake Waters by Bottom Deposits," Verh. Internat. Verein. Limnol. 14, 247-251 (1961).

Horie, S., "Paleolimnological Study on Ancient Lake Sediments in Japan, Verh. Internat. Verein. Limnol. 16, 274-281 (1966).

Hsu, P.H., "Fixation of Phosphate by Aluminum and Iron in Acidic Soils," Soil Sci. 99, 398-402 (1965).

Hsu, P.H., Jackson, M.L., "Inorganic Phosphate Transformations by Chemical Weathering in Soils as Influenced by pH," Soil Sci. 90, 16-24 (1960).

Hutchinson, G.E., "Limnological Studies in Connecticut: IV. Mechanism of Intermediary Metabolism in Stratified Lakes," Ecological Monographs 11, 21-60 (1941).

Hutchinson, G.E., "Treatise on Limnology, Vol. 1, John Wiley and Sons, New York 691-725 (1957).

Hutchinson, G.E., Wollack, A., "Studies on Connecticut Lake Sediments: II. Chemical Analysis of a Core from Linsley Pond North Bradford," Amer. J. Sci. 238, 493-517 (1940).

Jackman, R.H., Black, C.A., "Solubility of Iron, Aluminum, Calcium and Magnesium Inositol Phosphate at Different pH Values," Soil Sci. 72, 179 (1951).

Jackson, M.L., Soil Chemical Analysis, Prentice-Hall, Englewood Cliffs, New Jersey, 468 p. (1958).

Jenkins, D., Medsker, L.L., "Brucine Method for Determination of Nitrate in Ocean, Estuarine and Fresh Waters," Anal. Chem. 36, 610-616 (1964).

Jitts, H.R., The Adsorption of Phosphate by Estuarine Bottom Deposits," Australian J. Mar. Freshwater Res. 10, 7-21 (1959).

Juday, C., "Hydrography and Morphometry of the Inland Lakes of Wisconsin," Bull. Geol. Nat. Hist. Survey of Wis. 27, 137 p. (1914).

Juday, C.E., Birge, E.A., Meloche, V.W., "Chemical Analyses of the Bottom Deposits of Wisconsin Lakes II. Second Report," Trans. Wis. Acad. Sci. Arts Lett. 33, 99-114 (1941).

Kafkafi, U., Posner, A.M., Quirk, J.P., "Desorption of Phosphate from Kaolinite," Soil Sci. Soc. Amer. Proc. 31, 348-353 (1967).

Kaneshige, H.M., "Chemical Analysis of the Bottom Muds of Lake Mendota," M.S. Thesis, Civil Eng. Dept., Univ. of Wis. (1952).

Keeney, D.R., Konrad, J.G., Chester, G., "Nitrogen Distribution in Some Wisconsin Lake Sediments," J. Water Poll. Contr. Fed. 42, 411-417 (1970).

Kendall, R.L., "An Ecological History of the Lake Victoria Basin," Ecological Monographs 39, 121-176 (1969).

Kleckner, J., "The Role of the Bottom Fauna in Mixing Lake Sediments," M.S. Thesis, Univ. of Washington, 61 p. (1967).

Kleerekoper, H., "The Mineralization of Plankton," J. Fish Res. Bd. Canada 10, 283-291 (1953).

Krumbein, W.C., Garrels, R.M., "Origin and Classification of Chemical Sediments in Terms of pH and Oxidation-Reduction Potentials," J. Geol. 60, 1-33 (1952).

Kuznetsov, S.I., "A Study of the Size of Bacterial Populations and of Organic Matter Formation Due to Photo- Chemosynthesis in Water Bodies of Different Types," Verh. Internat. Verein. Limnol. 13, 156-169 (1958).

Laboratory Equipment Corporation, "Instrument Manual of Operation of LECO Carbon Analyzer," Laboratory Equipment Corporation. St. Joseph, Michigan, 20 p. (1959).

Lamb, H.H., "On the Nature of Certain Climatic Epochs which Differed from the Modern (1900-39) Normal," Proc. of WMO/UNESCO Rome Symposium on Climate Change, Paris (1963).

Larsen, G., Chilingar, G.V., Diagenesis of Sediments, Elsevier Publ. Co., New York, 536 p. (1967).

Lee, G.F., "Factors Affecting the Exchange of Material Between Water and Sediments," Paper presented before the Division of Water, Air and Waste Chemistry, Amer. Chem. Soc., New York, September (1969).

Lee, G.F., Personal Communication, Water Chemistry, Univ. of Wis. (1970).

Levihn, P., "A Sanitary Survey of the Yahara River and Bottom Muds of Lake Mendota," M.S. Thesis, Civil Eng. Dept., Univ. of Wis. (1951).

Lewis, C.F.M., McNeely, R.N., "Survey of Lake Ontario Bottom Deposits," Proc. of 10th Conf. on Great Lakes Research, 133-142 (1967).

Lindeman, R.L., "The Developmental History of Cedar Creek Bog, Minnesota," Amer. Midl. Nat. 25, 101-112 (1941).

Lindeman, R.L., "The Trophic-Dynamic Aspect of Ecology," Ecology 23, 399-418 (1942).

Lindsay, W.L., Moreno, E.C., "Phosphate Phase Equilibria in Soils," Soil Sci. Soc. Amer. Proc. 24, 177-182 (1960).

Livingstone, D.A., "On the Sigmoid Growth Phase in the History of Linsley Pond," Amer. J. of Sci. 255, 364-373 (1957).

Livingstone, D.A., Boykin, J.C., "Vertical Distribution of Phosphorus in Linsley Pond Mud," Limnol. & Oceanogr. 7, 57-62 (1962).

Ludlam, S.D., "Sedimentation in Cayuga Lake, New York," Limnol. & Oceanogr. 12, 618-632 (1967).

Lynn, D.C., Bonatti, E., "Mobility of Manganese in Diagenesis of Deep-Sea Sediments," Marine Geol. 3, 457-474 (1965).

Mackereth, F.J.H., "Chemical Investigation of Lake Sediments and Their Interpretation," Proc. Royal Soc. (B) 161, 295-309 (1965).

Mackereth, F.J.H., "Some Chemical Observations on Postglacial Sediments," Philosophical Trans. Royal Soc. of London (B) 250, 165-213 (1966).

Maher, L., Personal Communication, Geology Dept., Univ. of Wis. (1969).

Megard, R.O., "Planktonic Photosynthesis and the Environment of Calcium Carbonate Deposition in Lakes," Mitt. Internat. Verein. Limnol. 17, 94 (1969).

MacPherson, L.B., Sinclair, N.R., Hayes, F.R., "Lake Water and Sediment. III. The Effect of pH on the Partition of Inorganic Phosphate between Water and Oxidized Mud or its Ash," Limnol. & Oceanogr. 3, 318-326 (1958).

Mortimer, C.H., "The Exchange of Dissolved Substances between Mud and Water in Lakes," J. Ecology 29, 280-329 (1941).

Mortimer, C.H., "The Exchange of Dissolved Substances between Mud and Water in Lakes," J. Ecology 30, 147-201 (1942).

Morgan, J.J., Stumm, W., "The Role of Multivalent Metal Oxides in Limnological Transformations as Exemplified by Iron and Manganese," In Proc. Second Internat. Water Pollut. Res. Conf. (Tokyo) Pergamon Press, New York, 103-131 (1964).

Mortensen, J.L., Himes, F.L., "Soil Organic Matter," In F.E. Bear, ed., Chemistry of the Soil, 2nd ed. Reinhold, New York, 206-241 (1964).

Murray, R.C., "Recent Sediments of Three Wisconsin Lakes," Bull. Geol. Soc. Amer. 67, 883-910 (1956).

Murrmann, R.P., Peech, M., "Effect of pH on Labile and Soluble Phosphate in Soils," Soil Sci. Soc. Amer. Proc. 33, 205-210 (1969).

Nelson, P.R., Edmondson, W.T., "Limnological Effects of Fertilizing Bare Lake, Alaska," U.S. Fish and Wildlife Service, Fishery Bulletin 56, 413-436 (1955).

Nichols, M.S., Henkel, T., McNall, D., "Copper in Lake Muds from Lakes of the Madison Area," Trans. Wis. Acad. Sci. Arts & Lett. 38, 333-50 (1946).

Noland, W.C., "The Hydrography, Fish and Turtle Population of Lake Wingra," Trans. Wis. Acad. Sci. Arts & Lett. 40, 5-58 (1951).

Nriagu, J.O., "The Distribution of Sulfur and Iron in Lake Mendota Sediments," M.S. Thesis, Geology, Univ. of Wis., 102 p. (1967).

Nriagu, J.O., "The Distribution of Iron in Lake Sediments," Wis. Acad. Sci. Arts & Letts. 56, 153-164 (1967-1968).

Nriagu, J.O., "Sulfur Metabolism and the Sedimentary Environment: Lake Mendota, Wisconsin," Limnol. & Oceanog. 13, 430-439 (1968).

Nriagu, J.O., Bowser, C.J., "The Magnetic Spherules in Sediments of Lake Mendota, Wisconsin," Water Research 3, 833-842 (1969).

Nussman, D.G., "Trace Elements in the Sediments of Lake Superior," Ph.D. Thesis, Univ. of Michigan 243 p. (1965).

Nygaard, G., "On the Productivity of Five Danish Waters," Verh. Internat. Verein. Theor. Angew. Limnol. 12, 123-133 (1953).

Ogden, J.G. III., "Forest History of Ohio I. Radiocarbon Dates and Pollen Stratigraphy of Silver Lake, Logan County, Ohio," Ohio J. Sci. 66, 387-400 (1966).

Ogden, J.G., III, "Radiocarbon Determinations of Sedimentation Rates from Hard and Soft-Water Lakes in Northeastern North America," In Quaternary Paleoecology, E.J. Cushing and H.E. Wright, Jr. eds., Yale Univ. Press, New Haven, 175-183 (1967).

Ohle, W., "Die Ursachen der rasanten Seeneutrophierung," Verh. Internat. Verein. Theor. Angew. Limnol. 12, 373-382 (1955).

Olsen, S.R., Watanabe, F.S., "A Method to Determine a Phosphorus Adsorption Maximum of Soils as Measured by the Langmuir Isotherm" Soil Sci. Sco. Amer. Proc. 21, 144 (1957).

Olson R.V., "Iron," In C.A. Black, ed., Methods of Soil Analysis Part 2, Amer. Soc. Agronomy, Madison, Wis. 1179-1237 (1965).

Patrick, R., "The Diatoms of Linsley Pond, Connecticut," Proc. Acad. Nat. Sci. Philadelphia 95, 53-110 (1943).

Pennak, R.W., "Ecological and Radiocarbon Correlations in Some Colorado Mountain Lake and Bog Deposits," Ecology 44, 1-15 (1963).

Pennington, W., "Lake Sediments: The Bottom Deposits of the North Basin of Windermere, with Special Reference to the Diatom Succession," New Phytologist 42, 1-27 (1943).

Poff, R.J., Threinen, C.W., Surface Water Resources of Dane County, Wis. Conservation Dept., 61 p. (1962).

Pomeroy, L.R., Smith, E.E., Grant, C.M., "The Exchange of Phosphate between Estuarine Water and Sediments," Limnol. & Oceanogr. 10, 167-172 (1965).

Potzger, J.E., Van Engel, W.A., "Study of the Rooted Aquatic Vegetation of Weber Lake, Vilas County, Wisconsin," Trans. of Wis. Acad. of Sci. Arts and Lett. 34, 149-166 (1942).

Rakama, K., Sahama, T.G., Geochemistry, University of Chicago Press, 912 p. (1949).

Rawson, D.S., "Some Physical and Chemical Factors in the Metabolism of Lakes," In Problems of Lake Biology, Amer. Assoc. Adv. Sci. Publ. No. 10, 9-26 (1939).

Rittenberg, S.C., Emery, K.O., Orr, W.L., "Regeneration of Nutrients in Sediments of Marine Basins," Deep-Sea Res. 3, 23-45 (1955).

Rogers, M.A., "Carbohydrates in Aquatic Plants and Associated Sediments from Two Minnesota Lakes," Geochim, et Cosmochim. Acta 29, 183-200 (1965).

Rohlich, G.A., "Origin and Quantities of Plant Nutrients in Lake Mendota," In D.G. Frey, ed., *Limnology of North America*, 75-87 (1963).

Roth, F.,"On the Forestry Conditions of Northern Wisconsin." Wis. Geol. and Nat. Hist. Surv. Bull., 1, Econ. Series 1, Madison, 78 p. (1898).

Round, F.E., "The Diatoms of a Core from Esthwaite Water," New Phytologist 60, 43-59 (1961).

Round, F.E., "The Diatom Sequence in Lake Deposits: Some Problems of Interpretation," Verh. Internat. Verein. Limnol. 15, 1012-1020 (1964).

Sanchez, I., Personal Communication, Water Chemistry, Univ. of Wis. (1970).

Sarles, W.B., "Madison Lakes: Must Urbanization Destroy their Beauty and Productivity?" *In Trans. 1960 Algae and Metropolitan Wastes*, Robt. A. Taft Sanitary Engineering Center, Tech. Rept. W61-3, 10-18 (1961).

Savant, N.K., Ellis, R.,"Changes in Redox Potential and Phosphorus Availability in Submerged Soil," Soil Sci. 98, 388-394 (1964).

Sawyer, C.N., Lackey, J.B., Lenz, A.T., "Investigation of the Odor Nuisance Occurring in the Madison Lakes, Particularly Lakes Monona, Waubesa and Kegonsa from July 1943 to July 1944," Rept. to the Governor's Comm., State of Wis. (1944).

Serruya, C., "Problems of Sedimentation in the Lake of Geneva," Verh. Internat. Verein. Limnol. 17, 209-218 (1969).

Shah, R., Syers, J.K., Williams, J.D.H., Walker, T.W., "The Forms of Inorganic Phosphorus Extracted from Soils by N Sulfuric Acid," New Zeal. J. Agric. Res. 11, 184-192 (1968).

Spear, R.D., "The Release of Phosphorus from Lake Sediments," Ph.D. Thesis, Water Chemistry, Univ. of Wis., 231 p. (1970).

Stahl, J.B., "The Uses of Chironomids and other Midges in Interpreting Lake History," Mitt. Internat. Verein. Limnol. 17, 111-125 (1969).

Standard Methods for the Examination of Water and Wastewater, 12th Ed. APHA, AWWA, WPCF, New York, 769 p. (1965).

Steiner, J., Meloche, V.W., "A Study of Ligneous Substances in Lacustrine Materials, Trans. Wis. Acad. Sci. Arts Lett. 29, 389-402 (1935).

Stevenson, I.L., "Biochemistry of Soil," in F.E. Bear, ed., Chemistry of the Soil, 2nd ed. Reinhold, New York, 242-287 (1964).

Stewart, K.M., Rohlich, G.A., "Eutrophication--A Review," Publ. No. 34, Rept. to the State Water Quality Control Board, Calif. 188 p. (1967).

Stockner, J.G., Benson, W.W., "The Succession of Diatom Assemblages in the Recent Sediments of Lake Washington," Limnol. & Oceanogr. 12, 513-532 (1967).

Struthers, P.H., Seiling, D.H., "Effect of Organic Anions of Phosphate Precipitation by Iron and Aluminum as Influenced by pH," Soil Sci. 69, 205-213 (1950).

Swain, F.M., "Geochemistry of Some Quaternary Lake Sediments of North America," In H.E. Wright and D.G. Frey, eds., "The Quaternary of the United States, Princeton University Press 765-781 (1965).

Swenson, R.M., Cole, C.V., Sieling, D.H., "Fixation of Phosphate by Iron and Aluminum and Replacement by Organic and Inorganic Ions," Soil Sci. 67, 3-22 (1949).

Syers, J.K., Williams, J.D.H., Campbell, A.S., Walker, T.W., "The Significance of Apatite Inclusions in Soil Phosphorus Studies," Soil Sci. Soc. Amer. Proc. 31, 752-756 (1967).

Syers, J.K., Williams, J.D.H., Walker, T.W., "The Determination of Total Phosphorus in Soils and Parent Materials," New Zeal. J. Agric. Res. 11, 757-762 (1968).

Tandon, H.L.S., Kurtz, L.T., "Isotopic Exchange Characteristics of Aluminum- and Iron-bound Fractions of Soil Phosphorus," Soil Sci. Soc. Amer. Proc. 32, 799-802 (1968).

Thomas, E.A., "Die Eutrophierung von Seen und Flussen, deren Ursprung und Abwehr," Vjschr. Naturf. Ges. Zurich 107, 127-140 (1962).

Tippett, R., "An Investigation into the Nature of the Layering of Deep-water Sediments in Two Eastern Ontario Lakes," Canadian J. Bot. 42, 1693-1709 (1964).

Toyoda, Y., Horie, S., Saijo, Y., "Studies on the Sedimentation in Lake Biwa from the Viewpoint of Lake Metabolism," Mitt. Internat. Verein. Limnol. 14, 243-255 (1968).

Tressler, W.L., Domogalla, B.P., "Limnological Studies of Lake Wingra," Trans. Wis. Acad. Sci. Arts & Lett. 16, 331-351 (1931).

Turekian, K.K., "Rapid Technique for Determination of Carbonate Content of Deep-Sea Cores," Bull. Amer. Assoc. Petrol. Geol. 40, 2507-2509 (1940).

Twenhofel, W.H., "The Physical and Chemical Characteristics of the Sediments of Lake Mendota, A Freshwater Lake in Wisconsin," J. Sed. Petrol. 3, 68-76 (1933).

Twenhofel, W.H., "The Bottom Sediments of Lake Monona, a Fresh-Water Lake of Southern Wisconsin," J. Sediment. Petrol. 7, 67-77 (1937).

Twenhofel, W.H., Broughton, W.A., "The Sediments of Crystal Lake, an Oligotrophic Lake in Vilas County, Wisconsin," Amer. J. Sci. 237, 231-252 (1939).

Twenhofel, W.H., McKelvey, V.E., "Sediments of Devils Lake, Eutrophic-Oligotrophic Lake of Southern Wisconsin," J. Sediment. Petrol. 9, 105-121 (1939).

Twenhofel, W.H., McKelvey, V.E., "Sediments of Fresh-water Lakes," Amer. Assoc. Petrol. Geol. Bull. 25, 826-849 (1941)

Twenhofel, W.H., McKelvey, V.E., "The Sediments of Little Long Lake, Wisconsin," J. Sediment. Petrol. 12, 36-50 (1942).

Twenhofel, W.H., Carter, S.L., McKelvey, V.E., "The Sediments of Grassy Lake, Vilas County, A Large Bog Lake of Northern Wisconsin," Amer. J. Sci. 240. 529-546 (1942).

Twenhofel, W.H., McKelvey, V.E., Carter, S.A., Nelson, H., "The Sediments of Four Woodland Lakes, Vilas County, Wisconsin. I and II," Amer. J. Sci. 242, 19-44, 85-104 (1944).

Twenhofel, W.H., McKelvey, V.E., Nelson, H.F., Feray, D.E., "Sediments of Trout Lake, Wisconsin," Bull. Geol. Soc. Amer. 56, 1099-1142 (1945).

Vallentyne, J.R., "Sedimentary Chlorophyll Determination as Paleobotanical Method," Can. J. Botany 33, 304-313 (1955).

Vallentyne, J.R., "Sedimentary Organic Matter and Paleolimnology," Mitt. Internat. Verein. Limnol. 17, 104-110 (1969).

Vallentyne, J.R., Swabey, Y.S., "A Reinvestigation of the History of Lower Linsley Pond, Connecticut," Amer. J. Sci. 253, 313-340 (1955).

Veith, G.D., "The Role of Lake Sediments in the Water Chemistry of Toxaphene," M.S. Thesis, Water Chem. Dept., Univ. of Wis., 43 p. (1968).

Wang, W.C., Brabec, D.J., "Nature of Turbidity in the Illinois River," J. AWWA 61, 460-464 (1969).

Wentz, D.A., "Available Phosphorus in Lake Sediments," M.S. Thesis, Water Chem. Dept., Univ. of Wis., 106 p. (1967).

Wentz, D.A., Lee, G.F., "Sedimentary Phosphorus in Lake Cores - Analytical Procedure," Environ. Sci. & Technol. 3, 750-754 (1969a).

Wentz, D.A., Lee, G.F., "Sedimentary Phosphorus in Lake Cores--Observations on Depositional Pattern in Lake Mendota," Environ. Sci. & Technol. 3, 754-759 (1969b).

Whiteside, M.C., "Paleoecological Studies of Potato Lake and Environs." Ecology 46, 807-816 (1965).

Williams, J.D.H., Syers, J.K., Harris, R.F., Armstrong, D.E., "Adsorption and Desorption of Inorganic Phosphorus by Lake Sediments in a 0.1M NaCl System," Environ. Sci. & Technol. 4, 517-519 (1970).

Wright, H.E. Jr., "The Roles of Pine and Spruce in the Forest History of Minnesota and Adjacent Areas," Ecology 49, 937-955 (1968).

Zicker, E.L., Berger, K.C., Hasler, A.D., "Phosphorus Release from Bay Muds," Limnol. & Oceanogr. 1, 296-303 (1956).

Zobell, C.E., "Studies on Redox Potential of Marine Sediments," Bull. Am. Assoc. Petrol. Geol. 4, 477-513 (1946).

Zullig, H., "Die Bestimmung von Myxoxanhophyll in Bohrprofilen Zum Nachweis verganener Blaugenentfaltunger," Verh. Internat. Verein. Limnol. 14, 263-270 (1960).

APPENDIX A

Chemical Data on Lake Sediment Cores

The following information is prefaced to eliminate repetitive information in the tables and to acknowledge contributions from other investigators.

Notation on Tables

1. Depth of Sediment is depth below sediment-water interface.
2. Mean Density is the summation of the densities for all sections divided by numbers of sections in the core.
3. Standard Deviation is derived from 5 replicate samples using N-1 degrees of freedom.
4. Percent Solids is oven-dried sediment at 105° C.

Processing Sediment

All core samples are digested by $HF\text{-}HNO_3\text{-}HClO_4$ except Mendota (WC-89), Trout (WC-59) and Monona (WC-46) which were digested with $HClO_4\text{-}HNO_3$.

Acknowledgements

Determination	Core	Investigator
Acid Soluble P	WC-89	Wentz (1967)
Mn	WC-89	Delfino (1968)
Cu	WC-101	Sanchez (1970)

LAKE MENDOTA (WC - 89)

Date Collected: 26 October 1966 Location: 23.2m of Water, Center Deep Basin

Sect. No.	Depth of Sediment (cm)	% Solids	Total C	Org-C	CO_3-C	Org-N	NH_4-N	P	Acid Sol. P	Fe	Mn	Ca	Mg	K
			mg/g											
1	0- 5	11.1	118	80.5	37.5	9.95	--	1.79	--	18.9	1.50	125	13.4	--
2	5-10	16.2	127	89.5	37.5	9.38	--	1.79	0.88	18.9	1.28	125	12.0	9.85
3	10-15	19.4	114	82.2	31.8	8.73	0.41	1.31	0.82	22.8	1.08	106	10.5	10.3
4	15-20	19.0	93.5	63.3	30.2	7.01	0.46	1.64	0.72	24.4	1.12	101	10.4	11.2
5	20-25	17.3	99.0	67.2	31.8	6.49	0.54	1.68	0.86	22.8	1.12	106	10.6	10.6
6	25-30	16.4	97.0	64.3	32.7	6.65	0.52	1.96	0.98	22.3	1.20	109	10.6	10.5
7	30-35	16.1	99.0	66.9	32.1	7.06	0.49	1.74	0.88	21.0	1.04	107	10.9	9.93
8	35-40	16.3	109	74.2	34.8	8.15	0.49	1.55	0.96	18.2	0.96	116	10.7	8.77
9	40-45	14.9	112	76.0	36.0	8.20	0.49	1.23	0.70	16.4	0.72	120	10.6	8.83
10	45-50	14.2	119	81.5	37.5	8.44	0.47	1.16	0.73	16.4	0.72	125	10.3	8.60
11	50-55	11.9	121	88.3	32.7	8.38	0.50	1.09	0.64	15.5	0.64	109	9.70	8.53
12	55-60	12.9	122	83.9	38.1	8.13	0.40	0.99	0.59	13.8	0.56	128	10.4	7.70
13	60-65	13.0	114	70.8	43.2	5.74	0.34	0.89	0.60	12.3	0.48	144	11.2	7.43
14	65-70	12.9	113	62.0	51.0	7.00	0.41	0.90	0.61	9.83	0.44	170	12.1	6.13
15	70-75	13.9	113	54.3	58.7	7.31	0.35	0.92	0.65	8.50	0.40	196	10.4	3.00
16	75-80	13.2	126	68.4	57.0	8.05	0.41	0.97	0.60	5.90	0.32	192	9.00	2.75
17	80-85	12.9	128	72.2	55.8	7.10	0.39	0.87	0.61	7.50	0.34	186	9.55	2.10
18	85-90	13.1	123	62.7	60.3	6.82	0.35	0.85	0.62	6.82	0.38	201	8.90	1.99
19	90-95	13.7	122	66.3	55.7	7.16	0.40	0.87	0.59	6.30	0.34	186	10.6	2.30

Mean Density 1.08

LAKE MENDOTA (WC - 86)

Date Collected: 8 October 1966 Location: 18.3m of Water, University Bay

Sect. No.	Depth of Sediment (cm)	% Solids	Total C	Org-C	CO_3-C	P	Acid Sol. P	Fe	Mn	Ca	Mg	Al	K
			mg/g										
1	0- 5	11.2	110	78.2	31.8	1.60	0.770	22.3	1.06	106	13.7	46.2	11.3
2	5-10	24.7	106	76.6	29.4	1.32	0.583	23.4	0.880	98	14.3	50.4	11.9
3	10-15	25.0	92.5	62.2	30.3	1.42	0.556	21.9	0.867	101	14.0	47.9	12.1
4	15-20	23.5	91.5	63.3	28.2	1.17	0.591	22.0	0.780	94	13.3	47.8	12.0
5	20-25	24.2	109	80.8	28.2	1.21	0.587	21.0	0.705	94	15.1	46.4	11.7
6	25-30	22.8	111	79.2	31.8	1.13	0.548	20.1	0.737	106	14.9	45.6	11.2
7	30-35	23.1	108	76.2	31.8	1.30	0.548	17.2	0.655	106	14.3	43.6	11.1
8	35-40	27.9	119	86.3	32.7	1.13	0.543	16.6	0.605	109	14.7	43.2	10.9
9	40-45	22.9	104	71.6	32.4	1.10	0.529	16.2	0.570	108	14.7	42.3	11.1
10	45-50	22.6	106	67.0	39.0	1.00	0.529	14.3	0.534	130	14.8	39.8	9.50
11	50-55	24.1	119	71.3	47.7	1.02	0.532	12.5	0.512	159	16.8	37.2	6.53
12	55-60	23.1	---	--	65.4	1.11	0.605	9.21	0.521	218	16.8	29.1	6.53
13	60-65	18.8	153	76.5	76.5	0.945	0.567	5.80	0.460	255	13.4	15.9	3.04
14	65-70	17.8	146	69.5	76.5	1.11	0.569	7.55	0.453	255	12.9	15.2	3.10
15	70-75	17.8	126	51.0	75.0	1.01	0.593	8.08	0.430	250	12.6	14.7	2.71
16	75-80	18.1	128	56.6	71.0	0.815	0.540	7.15	0.435	238	12.8	17.9	3.67
17	80-85	18.8	136	64.0	72.0	0.787	--	7.15	0.437	240	13.0	17.8	3.57
18	85-90	19.1	130	52.4	77.6	0.949	0.538	6.45	0.420	259	12.8	14.8	3.10
19	90-95	18.2	131	55.1	75.9	1.07	0.571	6.39	0.420	253	12.7	16.0	2.80
20	95-100	15.5	128	53.2	74.8	0.963	0.594	6.60	0.437	249	12.5	14.0	3.00
Standard Deviation			$^{9}4.0$			$^{9}0.017$	$^{9}0.011$	$^{9}0.40$	$^{9}0.016$	$^{9}1.1$	^{9} 0.17	^{9} 2.3	$^{9}0.14$
Standard Deviation			$^{16}2.4$			$^{16}0.017$	$^{16}0.055$	$^{16}0.36$	$^{16}0.010$	$^{16}1.1$	^{16} 0.0	^{16} 0.32	$^{16}0.064$

LAKE MENDOTA (WC-84)

Date Collected: 8 October 1966 Location: 11.2m of Water, University Bay

Sect. No.	Depth of Sediment (cm)	% Solids	Total C	Org-C	CO_3-C	P	Fe	Mn	Ca	Mg	Al	K
			mg/g									
1	0- 5	27.1	128	100	28.0	1.19	20.1	0.626	93.3	17.5	38.5	10.6
2	5-10	28.7	122	94.3	27.7	1.18	20.5	0.626	92.3	17.4	38.2	11.0
3	10-15	31.0	109	82.6	26.4	1.10	20.0	0.602	87.8	17.5	41.3	11.7
4	15-20	35.1	103	78.7	24.3	1.09	21.5	0.602	81.0	17.4	43.0	12.6
5	20-25	34.3	127	99.6	27.4	1.13	21.3	0.644	91.5	17.6	40.8	11.7
6	25-30	30.2	132	102	29.6	1.10	20.2	0.667	98.5	16.3	38.2	10.5
7	30-35	31.6	136	106	29.9	1.12	19.8	0.714	99.8	16.5	37.0	10.7
8	35-40	34.0	134	105	29.4	1.05	19.2	0.703	98.0	16.1	36.5	10.3
9	40-45	34.3	130	100	29.8	1.05	19.0	0.667	99.5	15.9	36.4	10.6
10	45-50	29.4	148	119	29.4	1.06	17.0	0.588	98.0	15.3	33.0	9.90
11	50-55	29.4	154	120	34.5	1.06	15.0	0.524	115	15.2	30.5	8.90
12	55-60	29.0	148	102	46.2	0.990	12.9	0.506	154	16.5	26.7	8.15
13	60-65	25.6	147	91.5	55.5	0.976	11.0	0.497	185	17.1	19.8	6.77
14	65-70	27.0	150	89.0	61.0	0.968	9.35	0.488	203	16.5	16.6	5.20
15	70-75	25.6	155	91.4	63.6	0.928	8.93	0.486	212	16.9	15.6	5.13
16	75-80	27.5	167	89.0	78.0	0.908	6.70	0.450	260	15.8	9.80	2.83
17	80-85	23.9	167	88.0	79.0	0.886	6.25	0.454	263	16.2	9.40	2.73
18	85-90	25.2	165	88.8	76.2	0.818	6.33	0.447	254	15.9	9.04	2.60
19	90-95	26.0	163	92.5	70.5	0.820	7.38	0.506	235	16.1	9.52	2.60
20	95-100	28.2	173	94.0	77.0	0.838	6.85	0.501	257	16.5	9.61	2.78
Standard Deviation			$^{4}3.2$			$^{3}0.039$	$^{3}0.38$	$^{3}0.0010$	$^{3}0.63$	^{3} 0.16	$^{3}0.37$	$^{3}0.050$
Standard Deviation			$^{14}4.0$			$^{13}0.017$	$^{13}0.27$	$^{13}0.0020$	^{13} 22	^{13} 0.95	$^{13}0.20$	$^{13}0.54$

LAKE MENDOTA (WC-82)

Date Collected: 8 October 1966 Location: 3.8 m of water, University Bay

Sect. No.	Depth of Sediment (cm)	% Solids	Total C	Org-C	CO_3-C	P	Fe	Mn	Ca	Mg	Al	K
			mg/g									
1	0-5	26.6	105	77.0	28.0	0.806	13.1	0.510	93.3	17.6	34.4	10.7
2	5-10	34.4	106	79.2	26.8	0.868	13.1	0.500	89.5	15.3	34.4	10.3
3	10-15	29.8	119	64.0	55.0	0.688	9.52	0.491	183	13.5	24.7	6.55
4	15-20	27.1	134	69.2	64.8	0.518	4.80	0.492	216	10.8	11.0	2.95
5	20-25	31.6	145	76.6	68.4	0.550	4.33	0.459	228	10.6	10.7	2.37
6	25-30	38.6	122	55.5	66.5	0.560	5.03	0.422	222	13.5	12.5	3.74
7	30-35	38.2	121	43.0	78.0	0.632	3.58	0.400	260	13.5	12.5	3.33
8	35-40	33.6	125	43.9	81.1	0.416	3.80	0.386	271	12.0	10.7	2.57
9	40-45	33.8	123	48.9	75.1	0.454	4.27	0.374	251	12.9	12.2	3.15
10	45-50	34.1	126	65.7	60.3	0.490	4.73	0.374	201	11.8	12.2	3.22
11	50-55	45.3	108	44.2	63.8	0.410	4.85	0.366	213	17.3	15.3	4.81
12	55-60	53.1	--	--	37.4	0.394	6.04	0.344	--	18.2	19.3	7.25
13	60-65	48.3	102	45.4	56.6	0.455	5.55	0.378	189	18.7	16.3	5.59
14	65-70	43.1	119	55.9	63.1	0.472	5.17	0.410	211	15.4	13.5	3.96
15	70-75	44.4	114	54.5	59.5	0.470	5.17	0.397	198	16.1	14.0	4.59
16	75-80	52.4	93.4	46.4	47.0	0.468	5.42	0.368	157	17.4	17.0	6.27
17	80-85	52.3	96.2	56.0	40.2	0.428	5.80	0.364	134	16.2	17.0	6.66
18	85-90	53.5	91.0	46.7	44.3	0.408	5.78	0.342	148	19.5	18.0	7.07
19	90-95	59.5	81.8	37.8	44.0	0.392	5.05	0.306	147	20.0	17.7	7.05
20	95-100	61.8	86.1	42.6	43.5	0.440	5.91	0.315	145	21.1	19.1	7.42
Standard Deviation			$^{5}3.0$			$^{3}0.019$	$^{3}0.23$	$^{3}0.0011$	$^{3}4.3$	$^{3}0.54$	$^{3}0.34$	$^{3}0.39$
Standard Deviation			$^{15}3.2$			$^{13}0.011$	$^{13}0.0028$	$^{13}0.0028$	$^{13}4.5$	$^{13}0.48$	$^{13}0.0$	$^{13}0.11$

LAKE MENDOTA (WC-95)

Date Collected: 14 November 1968 Location: 23 m of Water, Center Deep Basin

Sect. No.	Depth of Sediment (cm)	% Solids	Total C	Org-C	CO_3-C	P	Fe	Mn	Ca	K	Al
						mg/g					
52	0-11	12.4	122	92.4	29.6	1.86	--	1.09	98.5	10.8	38.2
51	11-22	20.7	122	88.7	33.3	2.06	--	1.12	111	10.8	38.5
50	22-42	15.1	117	87.4	29.6	1.99	22.0	1.23	98.5	10.8	41.5
49	42-62	15.8	121	88.0	33.0	1.47	16.3	0.712	110	8.78	30.0
48	62-82	12.3	133	75.4	57.6	0.940	10.0	0.433	192	3.11	13.0
47	82-102	12.8	130	65.0	65.0	0.880	9.25	0.400	217	2.23	10.4
43	157-177	15.6	127	62.1	64.9	0.913	7.75	0.365	216	2.43	11.4
41	197-217	16.1	123	59.5	63.5	0.878	7.75	0.402	212	2.20	10.8
39	237-257	17.2	136	68.5	67.5	0.873	6.80	0.370	225	2.01	11.7
35	312-332	17.5	141	77.2	63.8	0.875	5.73	0.338	213	2.01	10.4
31	394-414	16.9	133	68.9	64.1	0.834	5.10	0.332	214	1.68	8.00
27	474-494	16.5	131	66.9	64.1	0.801	5.13	0.330	214	1.55	7.25
23	554-574	17.4	123	61.5	61.5	0.820	5.20	0.330	205	1.27	6.55
18	639-659	17.9	131	69.9	61.1	0.866	6.15	0.352	204	1.79	8.05
14	718-738	20.7	136	68.2	67.8	0.852	5.95	0.395	226	1.69	8.00
12	758-778	19.9	132	66.9	65.1	0.870	6.00	0.364	217	2.09	8.80
10	798-818	19.2	122	59.0	63.0	0.825	5.73	0.332	210	2.00	8.55
6	880-900	17.9	118	63.5	54.5	0.806	6.60	0.328	182	2.30	9.85
3	935-950	16.3	119	50.6	68.4	0.806	5.45	0.400	228	1.68	8.25
1	970-990	20.8	108	53.0	55.0	0.820	6.90	0.360	183	2.04	10.2

Mean Density 1.03

Standard Deviation ^{14}6.4

MONONA (WC - 46)

Collected: 30 June 1966
Location: 15.9m of Water, North Central Basin

Section Number	Depth of Sediment (cm)	P	Fe	Mn	Ca	Mg	K	Al
		mg/g						
1	0- 5	1.83	18.5	0.760	113	14.0	2.97	1.90
2	5-10	1.71	17.0	0.717	114	12.7	2.77	1.86
3	10-15	1.51	17.4	0.673	122	11.4	2.69	1.86
4	15-20	1.60	20.3	0.720	121	11.0	2.85	1.91
5	20-25	1.66	20.0	0.740	114	11.0	2.89	2.06
6	25-30	1.77	20.1	0.812	108	10.5	3.04	2.26
7	30-35	1.92	19.3	0.882	106	10.4	3.31	2.44
8	35-40	1.44	16.5	0.784	144	12.2	2.57	1.84
9	40-45	1.34	13.2	0.695	172	11.5	1.76	1.30
10	45-50	1.33	12.0	0.707	157	11.0	1.76	1.37
11	50-55	1.17	10.9	0.494	172	11.5	1.80	1.37
12	55-60	1.17	10.0	0.477	182	11.5	1.19	1.09
13	60-65	1.22	7.70	0.458	239	12.1	0.82	0.63
14	65-70	1.23	7.80	0.433	220	11.0	0.76	0.59
15	70-75	1.12	7.33	0.418	223	11.2	0.67	0.58
16	75-80	1.06	7.23	0.383	219	11.0	0.71	0.58
17	80-85	0.910	6.50	0.376	212	10.6	0.69	0.57
18	85-90	0.785	5.30	0.364	204	10.2	0.63	0.54
19	90-95	0.756	5.53	0.377	191	9.55	0.62	0.52
20	95-100	0.744	5.20	0.372	187	9.35	0.60	0.50
21	100-105	0.764	5.73	0.376	191	9.55	0.64	0.69

LAKE MONONA (WC - 101)

Date Collected: 10 June 1969 Location: 21 m of Water, Deep Area

Sect. No.	Depth of Sediment (cm)	% Solids	Total C	Org-C	CO_3-C	P	Fe	Mn	Ca	Mg	K	Al	$S^{=}$-S	NH_4-N	Cu
										mg/g					
1	0- 5	11.8	136	101	35.4	1.74	18.2	0.807	118	17.4	9.04	31.4	2.36	0.22	
2	5-10	14.9	133	99.0	34.0	1.76	17.8	0.809	113	16.0	9.05	31.1	2.22	0.30	0.246
3	10-15	15.0	131	102	29.5	1.67	17.6	0.742	98.2	14.5	9.24	32.2	--	0.20	
4	15-20	15.8	136	107	29.1	1.71	17.4	0.709	97.0	13.1	8.67	31.2	2.32	0.62	0.271
5	20-25	17.9	139	107	32.1	1.67	15.6	0.714	107	12.7	8.20	29.8	--	0.67	
6	25-30	19.1	136	102	33.6	1.65	16.6	0.737	112	13.3	8.26	31.1	1.98	0.67	0.260
7	30-35	19.2	129	98.6	30.4	1.60	17.8	0.752	102	13.1	8.56	32.2	--	0.84	
8	35-40	21.9	124	97.4	26.6	1.63	17.6	0.770	88.7	12.3	9.26	33.9	2.50	0.81	0.357
9	40-45	23.0	124	94.5	29.5	1.64	15.9	0.809	98.3	12.5	9.13	33.1	--	0.83	
10	45-50	22.7	125	96.6	28.4	1.58	16.1	0.802	94.5	12.2	8.98	32.8	--	0.86	0.410
11	50-55	22.4	127	98.2	28.8	1.70	17.2	0.852	96.0	13.0	9.13	35.2	1.50	0.88	
12	55-60	23.2	123	97.0	26.0	1.70	15.9	0.857	86.5	11.5	9.20	35.8	1.59	0.88	0.653
13	60-65	22.8	125	95.6	29.4	1.51	16.2	0.818	98.1	13.2	9.29	35.0	2.04	0.87	
14	65-70	23.6	120	93.1	26.9	1.77	17.5	0.883	89.5	13.1	9.84	37.0	1.97	0.94	0.588
15	70-75	22.1	113	86.1	26.9	1.83	17.8	0.882	89.5	13.5	9.90	37.2	--	0.88	
16	75-80	20.6	121	92.2	28.8	1.48	17.4	0.793	95.6	12.8	9.08	34.5	2.39	0.93	0.358
17	80-85	22.2	118	86.0	32.0	1.32	16.7	0.702	107	12.9	9.04	34.5	--	0.96	0.106
18	85-90	23.7	120	91.9	28.1	1.45	15.7	0.764	93.7	11.9	9.06	33.8	2.58	0.90	0.055
19	90-95	22.7	133	97.2	35.8	1.69	13.1	0.865	120	12.4	7.05	25.0	--	--	0.040
20	95-100	--	136	101	35.2	1.43	10.9	0.734	118	11.7	6.21	22.2	--	--	0.039
Mean Density		1.09													
Standard Deviation			$^{6}2.4$			$^{3}0.030$	$^{3}0.73$	$^{3}0.0038$	$^{3}4.5$	$^{3}0.59$	$^{3}0.066$	$^{3}0.29$			$^{2}0.0038$
Standard Deviation			$^{16}0.90$			$^{13}0.11$	$^{13}1.61$	$^{13}0.0070$	$^{13}12$	$^{13}1.5$	$^{13}0.91$	$^{13}0.042$		$^{17}0.050$	$^{17}0.0059$

LAKE WINGRA (WC - 92)

Date Collected: 10 May 1968   Location: 3.4 m of Water

Sect. No.	Depth of Sediment (cm)	% Solids	Total C	Org-C	CO_3-C	Org-N	NH_4-N	P	Acid Sol-P	Fe	Mn	Ca	Mg	K	Al
			mg/g												
1	0- 5	8.8	144	71.4	72.6	8.34	0.092	0.633	0.277	8.82	0.560	242	10.9	5.54	29.9
2	5-10	16.1	148	78.0	70.0	8.17	0.048	0.641	0.283	8.70	0.568	233	10.8	5.54	30.6
3	10-15	20.1	146	78.5	67.5	7.90	0.061	0.578	0.312	8.22	0.548	225	10.5	5.23	30.9
4	15-20	21.7	144	74.4	69.6	7.77	0.073	0.619	0.302	8.25	0.562	232	10.6	5.50	32.0
5	20-25	21.2	134	64.0	70.0	7.08	0.077	0.538	0.284	8.04	0.562	233	10.2	5.67	31.3
6	25-30	22.3	125	55.0	70.0	7.03	0.14	0.486	0.283	7.82	0.578	233	9.30	5.45	30.2
7	30-35	23.1	128	59.0	69.0	7.20	0.14	0.480	0.300	7.70	0.578	230	9.75	5.48	30.0
8	35-40	23.4	132	57.5	74.5	6.63	0.18	0.461	0.294	8.26	0.578	248	9.43	5.38	31.0
9	40-45	23.8	137	67.0	70.0	6.74	0.15	0.450	0.311	7.85	0.572	233	9.43	5.18	30.4
10	45-50	24.7	134	65.0	69.0	6.60	0.18	0.482	0.311	8.05	0.607	230	9.55	5.22	30.4
11	50-55	23.7	142	67.5	74.5	7.96	0.21	0.507	0.359	7.96	0.622	248	9.10	5.45	30.5
12	55-60	23.8	138	69.0	69.0	7.36	0.21	0.596	0.373	7.75	0.637	230	8.84	5.23	29.2
13	60-65	21.1	145	70.5	74.5	8.44	0.18	0.534	0.396	6.69	0.625	248	8.00	4.41	25.7
14	65-70	17.5	169	87.5	81.5	10.3	0.22	0.576	0.381	3.95	0.400	272	7.05	1.55	14.1
15	70-75	16.8	177	92.0	85.0	10.6	0.20	0.539	0.394	2.50	0.312	283	6.15	0.82	9.0
16	75-80	18.6	168	72.5	95.5	8.98	0.21	--	--	2.00	0.276	318	6.02	0.53	8.2
17	80-85	18.4	174	78.1	95.9	9.88	0.23	0.461	0.371	1.89	0.287	319	6.00	0.52	8.0
18	85-90	20.5	176	80.5	95.5	9.65	0.23	0.470	0.364	2.30	0.275	318	6.40	0.76	9.1
Mean Density		1.13													
Standard Deviation			$^{5}7.0$			$^{5}0.36$	$^{4}0.009$	$^{5}0.0032$	$^{5}0.0010$	$^{5}0.20$	$^{5}0.0$	$^{5}4.4$	$^{5}0.22$	$^{5}0.13$	$^{5}0.28$
Standard Deviation			$^{16}8.6$				$^{11}0.014$	$^{11}0.006$	$^{16}0.0087$	$^{11}0.33$	$^{11}0.012$	$^{16}8.0$	$^{11}0.22$	$^{11}0.030$	$^{11}0.21$
Standard Deviation							$^{15}0.040$	$^{16}0.081$		$^{16}0.078$	$^{16}0.0$		$^{16}0.59$	$^{16}0.059$	$^{16}0.17$

DEVILS LAKE (WC-75)

Date Collected: 13 August 1966 Location: 13.1 m of Water, Center of South Basin

Sect. No.	Depth of Sediment (cm)	% Solids	Org-C	P	Fe	Mn	Ca	Mg	K	Al
			mg/g							
1	0-5	14.6	73.2	2.39	37.1	0.454	2.50	4.75	13.9	90.3
2	5-10	15.2	--	1.41	33.8	0.351	2.18	4.85	13.9	92.4
3	10-15	15.9	88.8	1.24	32.2	0.312	2.20	4.84	12.5	95.4
4	15-20	14.4	121	1.24	27.5	0.296	1.95	4.18	8.98	89.2
5	20-25	13.3	118	1.17	28.2	0.283	1.91	4.13	8.92	86.0
6	25-30	17.7	109	1.12	26.5	0.276	1.99	4.28	10.1	87.4
7	30-35	14.1	108	--	25.4	0.284	2.13	4.32	10.6	86.3
8	35-40	14.8	102	1.11	27.7	0.265	1.82	4.33	9.96	82.5
9	40-45	17.5	120	1.05	28.7	0.260	1.91	4.19	9.24	82.4
10	45-50	18.3	115	1.06	27.6	0.258	1.52	4.20	9.23	82.4
11	50-55	14.7	118	1.02	27.9	0.261	1.85	4.31	8.66	82.6
12	55-60	12.7	128	1.00	24.6	0.237	1.58	3.79	8.93	74.6
13	60-65	12.3	150	0.894	21.8	0.221	1.25	3.41	8.57	65.3
14	65-70	12.2	139	0.904	22.7	0.220	1.60	3.35	8.61	63.5
15	70-75	15.7	134	0.934	23.4	0.227	1.70	3.51	8.61	65.4
16	75-80	12.6	141	0.924	22.4	0.216	1.87	3.37	9.10	62.7
17	80-85	11.9	158	0.984	21.6	0.216	1.78	3.37	8.50	58.5
18	85-90	11.9	152	0.988	20.2	0.209	1.91	3.32	8.65	58.7
19	90-95	13.3	143	0.936	21.2	0.217	1.81	3.41	8.78	58.9
Mean Density		1.06								
Standard Deviation			$^{6}3.5$	$^{5}0.023$	$^{5}0.94$	$^{5}0.0023$	$^{5}0.087$	$^{5}0.17$	$^{5}0.45$	$^{5}4.2$
Standard Deviation			$^{16}4.7$							

TROUT LAKE (WC-59)

Date Collected: 9 August 1966 Location: 32.6 m of Water, South Bay

Sect. No.	Depth of Sediment (cm)	% Solids	Org-C	Org-N	NH_4-N	P	Acid Sol. P	Fe	Mn	Ca	Mg	K
							mg/g					
1	0-5	3.05	161	18.2	0.24	7.88	7.00	66.3	4.02	3.52	2.50	1.47
2	5-10	4.05	148	15.8	0.16	6.73	5.81	57.2	3.46	3.10	2.72	1.67
3	10-15	4.29	135	15.0	0.18	5.05	4.55	52.5	2.13	3.00	2.58	1.42
4	15-20	6.06	141	13.8	0.18	5.37	5.20	51.3	2.37	2.98	2.65	1.70
5	20-25	6.47	144	14.2	0.23	5.00	4.26	50.7	2.30	2.98	2.28	1.22
6	25-30	6.64	147	14.4	0.25	5.21	4.69	53.7	2.58	3.10	2.20	1.06
7	30-35	6.78	175	16.5	0.26	5.20	4.85	61.8	2.69	4.30	2.30	1.02
8	35-40	6.17	187	18.0	0.24	2.96	2.80	51.0	1.94	4.00	2.27	1.04
9	40-45	5.99	194	18.4	0.24	2.15	1.93	44.1	1.59	4.46	2.31	1.10
10	45-50	6.34	155	15.1	0.24	4.40	4.35	43.0	2.37	2.93	1.73	0.80
11	50-55	6.65	170	16.1	--	6.70	6.10	60.0	3.25	3.86	2.23	0.98
12	55-60	6.79	183	17.1	0.29	5.18	4.68	60.5	2.58	3.36	2.49	1.22
13	60-65	7.61	179	16.7	0.27	5.40	4.93	60.0	2.72	4.85	2.66	1.16
14	65-70	7.42	202	17.8	0.29	4.30	3.55	58.8	2.43	4.62	2.72	1.30
15	70-75	7.35	202	17.7	0.30	4.50	3.93	62.8	2.58	3.60	2.72	1.39
16	75-80	7.73	208	17.9	0.31	4.50	4.43	59.3	2.62	3.35	2.82	1.52
17	80-85	8.05	202	18.2	0.34	5.50	5.05	64.5	2.90	3.46	2.93	1.68
18	85-90	8.18	211	17.9	0.33	4.07	2.85	58.1	2.13	3.46	2.90	1.56
19	90-95	8.02	203	18.3	0.33	3.00	2.33	54.0	1.97	3.33	2.70	1.48
20	95-100	8.32	180	16.1	0.31	5.50	5.35	60.0	2.90	3.70	2.56	1.48
21	100-105	8.24	166	16.1	0.22	6.01	5.80	58.4	2.50	3.36	2.51	1.47

Mean Density 1.04

TROUT LAKE (WC-60)

Date Collected: 9 August 1966 Location: 26 m of Water, North Bay

Sect. No.	Depth of Sediment (cm)	% Solids	Org-C	P	Fe	Mn	Ca	Mg	K	Al
			mg/g							
1	0-5	4.18	144	9.94	69.5	3.85	2.26	3.01	4.34	25.8
2	5-10	6.63	134	7.43	58.9	2.86	2.49	3.31	4.95	26.8
3	10-15	6.85	142	4.78	47.3	1.96	2.31	3.15	4.74	26.5
4	15-20	7.54	135	4.33	45.8	1.98	2.19	3.29	4.98	27.0
5	20-25	7.27	145	4.25	46.3	1.72	2.32	3.32	4.12	23.5
6	25-30	7.08	167	3.65	44.8	1.70	2.79	3.35	4.19	25.5
7	30-35	6.67	209	2.15	42.3	1.34	3.35	2.93	3.76	23.0
8	35-40	7.40	200	2.08	41.0	1.30	3.29	3.16	3.69	22.5
9	40-45	7.48	203	1.78	38.7	1.18	3.74	3.22	3.89	23.9
10	45-50	7.57	200	2.68	48.9	1.51	3.29	3.31	3.82	23.7
11	50-55	7.66	217	2.14	50.0	1.38	3.39	3.64	4.33	26.7
12	55-60	7.37	226	1.55	44.3	1.21	3.45	4.00	5.14	30.5
13	60-65	8.40	237	1.44	36.7	1.12	3.61	4.03	5.41	31.4
14	65-70	8.06	232	1.16	32.5	1.03	4.25	4.17	5.85	36.0
15	70-75	8.10	228	1.36	34.3	1.05	3.60	4.33	6.20	37.0
16	75-80	8.13	220	1.67	42.5	1.23	4.19	4.24	5.79	34.5
17	80-85	7.80	229	1.55	36.1	1.21	3.99	3.95	5.84	32.5
18	85-90	8.26	240	1.27	34.4	1.07	3.90	3.89	5.55	30.3
19	90-95	8.54	240	2.98	43.9	1.56	3.85	4.00	5.40	29.5
20	95-100	7.78	234	1.46	36.0	1.09	3.72	3.69	4.80	27.0
Mean Density		1.02								
Standard Deviation			$^{5}4.9$	$^{7}0.035$	$^{7}5.9$	$^{7}0.025$	$^{7}0.13$	$^{7}0.32$	$^{7}0.099$	$^{7}0.29$
Standard Deviation			$^{16}5.3$	$^{13}0.022$	$^{13}1.9$	$^{13}0.011$	$^{13}0.21$	$^{13}0.23$	$^{13}0.20$	$^{13}0.22$

LITTLE ST. GERMAIN (WC - 92)

Date Collected: 12 March 1967 Location: 15.6 m of Water, Center of West Bay

Sect. No.	Depth of Sediment (cm)	% Solids	Org-C	P	Fe	Mn	Ca	Mg	K	Al
			mg/g							
1	0- 5	2.45	143	10.1	102	1.61	0.48	2.04	3.15	13.8
2	5-10	5.06	126	11.1	108	1.39	0.43	1.91	3.04	13.2
3	10-15	6.15	123	9.20	99.3	1.39	0.67	3.13	4.09	16.9
4	15-20	6.19	141	7.36	81.7	1.27	0.70	2.77	3.87	15.7
5	20-25	6.46	143	7.60	77.5	1.07	0.73	2.54	3.80	15.7
6	25-30	6.56	150	7.12	73.5	0.90	0.87	2.86	3.95	16.2
7	30-35	6.15	151	7.80	83.0	1.15	0.62	2.26	3.65	16.1
8	35-40	6.52	183	10.5	88.5	1.41	0.54	2.02	2.80	12.3
9	40-45	5.85	222	14.7	102	2.09	0.55	1.69	1.93	9.15
10	45-50	5.53	210	13.9	106	2.19	0.56	1.51	1.85	8.65
11	50-55	5.49	191	10.8	89.0	1.76	0.53	1.87	2.08	8.94
12	55-60	6.13	185	11.7	97.3	1.80	0.54	1.42	1.83	8.17
13	60-65	6.09	218	14.5	108	2.55	0.44	1.51	1.94	8.64
14	65-70	6.32	224	15.1	109	2.34	0.50	1.61	2.20	9.62
15	70-75	6.26	231	16.5	117	2.74	0.55	1.61	2.15	9.68
16	75-80	6.36	225	16.3	116	2.80	0.42	1.44	1.88	8.75
17	80-85	6.49	228	15.8	113	2.54	0.44	1.78	2.30	10.3
18	85-90	6.80	240	15.4	107	2.60	0.46	1.87	2.65	11.9
Mean Density		1.02								
Standard Deviation			$^{3}2.2$	$^{18}0.13$	$^{18}0.0$	$^{18}0.011$	$^{18}0.014$	$^{18}0.079$	$^{18}0.016$	$^{18}0.091$

LITTLE ST. GERMAIN (WC - 56)

Date Collected: 9 August 1966 Location: 7.0 m of Water, South Bay

Sect. No.	Depth of Sediment (cm)	% Solids	Org-C	P	Fe	Mn	Ca	Mg	K	Al
			mg/g							
1	0-15	3.10	215	7.46	67.7	0.540	1.19	2.43	4.02	16.8
2	15-20	3.84	223	7.45	64.4	0.506	1.18	2.43	4.09	16.8
3	20-25	4.23	226	7.50	65.0	0.514	1.73	2.48	4.15	17.9
4	25-30	4.39	236	6.42	56.0	0.414	1.71	2.62	4.18	17.9
5	30-35	5.44	232	4.31	40.6	0.306	1.47	2.70	4.51	17.9
6	35-40	6.05	210	4.83	39.1	0.284	1.10	2.35	4.27	18.6
7	40-45	6.66	202	3.88	34.5	0.270	1.54	2.16	3.58	16.6
8	45-50	6.17	212	3.88	34.0	0.270	0.921	1.89	3.51	16.4
9	50-55	5.68	212	4.13	32.7	0.273	0.910	1.82	3.07	14.1
10	55-60	5.73	198	4.61	31.3	0.287	0.765	1.68	2.84	14.1
11	60-65	6.38	215	6.79	42.1	0.377	0.682	1.71	3.09	14.1
12	65-70	5.90	233	9.88	50.7	0.571	0.620	1.20	1.60	10.7
13	70-75	6.28	232	10.1	51.2	0.672	0.724	1.20	2.05	9.60
14	75-80	6.21	237	9.65	49.5	0.562	0.631	1.07	1.26	9.50
15	80-85	6.28	235	12.1	56.2	0.648	0.532	1.06	1.31	9.00
Mean Density		1.02								
Standard Deviation			^{12}2.8	11 0.22	11 0.75	^{11}0.0083	^{11}0.71	^{11}2.0	^{11}0.080	^{11}0.0

LAKE MINOCQUA (WC-51)

Date Collected: 8 August 1966 **Location:** 10.7 m of Water, N. W. Bay

Sect. No.	Depth of Sediment (cm)	% Solids	Org-C	P	Fe	Mn	Ca	Mg	K	Al
			mg/g							
1	0- 5	5.06	148	7.94	54.4	0.804	2.09	3.37	7.42	26.2
2	5-10	6.89	160	5.77	50.9	0.665	2.42	3.67	8.70	30.2
3	10-15	7.09	171	3.68	45.8	0.540	2.49	3.58	9.24	30.0
4	15-20	7.93	173	2.84	43.6	0.495	2.49	3.55	9.24	29.4
5	20-25	8.75	180	2.94	44.3	0.503	2.64	3.52	9.41	29.4
6	25-30	8.68	170	3.38	43.5	0.567	2.60	3.73	9.72	30.2
7	30-35	8.54	187	3.01	41.8	0.542	2.65	3.92	8.87	29.6
8	35-40	8.40	186	2.75	41.1	0.506	2.66	3.92	8.83	29.6
9	40-45	8.57	179	3.16	41.1	0.544	2.57	3.84	9.05	30.3
10	45-50	8.71	189	3.00	40.9	0.512	2.45	3.73	8.46	30.2
Mean Density		1.04								
Standard Deviation			^{4}3.7							

LAKE MINOCQUA (WC-52)

Date Collected: 8 August 1966 Location: 13.7 m of Water, Middle of S.W. Bay

Sect. No.	Depth of Sediment (cm)	% Solids	Org-C	P	Fe	Mn	Ca	Mg	K	Al
			mg/g							
1	0- 5	5.00	139	9.23	60.3	1.97	1.58	3.36	5.20	30.5
2	5-10	6.45	123	9.[illegible]	70.8	1.90	1.55	3.30	5.86	33.4
3	10-15	6.66	119	7.07	61.5	1.59	1.79	3.32	6.96	37.5
4	15-20	7.41	125	5.18	51.0	1.26	2.05	3.34	7.39	38.1
5	20-25	7.62	131	5.60	49.3	1.23	2.04	3.31	7.32	38.3
6	25-30	7.80	143	6.40	47.8	1.30	2.06	2.71	7.31	26.0
7	30-35	7.80	153	5.82	40.8	1.25	2.13	2.09	3.68	16.4
8	35-40	7.28	154	6.21	40.0	1.20	1.49	2.05	3.39	15.2
9	40-45	7.19	150	7.02	41.3	1.21	1.52	1.88	3.20	15.3
10	45-50	7.59	151	6.74	39.3	1.24	1.35	1.72	3.02	13.3
11	50-55	7.31	156	8.06	46.3	1.38	1.30	1.85	2.89	13.0
12	55-60	6.64	146	8.49	48.8	1.20	1.32	1.65	2.58	10.5
13	60-65	7.24	153	9.19	53.5	1.55	1.06	1.78	2.64	10.5
Mean Density		1.02								
Standard Deviation			^{4}3.8							

WEBER LAKE (WC-66)

Date Collected: 11 August 1966 Location: 12.6 m of Water, Center of Lake

Sect. No.	Depth of Sediment (cm)	% Solids	Org-C	P	Fe	Mn	Ca	Mg	K	Al
						mg/g				
1	0- 5	3.82	246	2.85	14.2	0.253	0.830	2.90	8.15	33.0
2	5-10	4.82	269	2.83	12.6	0.228	0.656	2.63	7.31	30.1
3	10-15	4.12	312	3.40	9.87	0.209	0.502	1.91	5.11	24.0
4	15-20	5.11	299	3.15	10.9	0.210	0.552	2.38	6.00	28.8
5	20-25	5.30	264	3.14	11.7	0.224	0.595	2.66	6.95	32.6
6	25-30	5.42	289	3.27	11.3	0.234	0.589	2.56	6.64	26.5
7	30-35	5.69	322	3.38	10.2	0.256	0.680	2.07	5.75	22.6
8	35-40	4.75	320	3.39	10.5	0.290	0.730	1.95	5.47	21.9
9	40-45	.5.25	329	3.81	11.3	0.314	0.838	1.87	5.65	23.9
10	45-50	5.00	325	3.95	10.5	0.300	0.678	2.18	5.29	26.8
11	50-55	4.82	310	3.09	10.6	0.300	0.845	2.58	6.33	31.5
12	55-60	4.91	367	2.71	10.2	0.320	1.08	1.99	4.75	25.0
13	60-65	5.38	362	2.90	10.3	0.318	1.26	2.10	4.97	25.1
14	65-70	6.01	337	3.20	11.4	0.320	1.12	2.29	5.51	28.8
15	70-75	--	--	--	--	--	--	--	--	--
16	75-80	5.14	299	3.26	12.7	0.286	0.951	2.89	6.65	34.7
17	80-85	5.54	300	2.89	12.9	0.286	0.860	2.80	6.66	33.0
18	85-90	5.44	300	3.09	12.9	0.292	0.947	1.43	6.68	34.2
19	90-95	5.44	319	3.09	12.1	0.290	0.920	1.61	5.97	30.7
Mean Density		1.02								
Standard Deviation			^{6} 14	^{9}0.029	^{9}0.26	^{9}0.0	^{9}0.038	^{9}0.16	^{9}0.13	^{9}0.71
Standard Deviation			^{13}3.9							

LITTLE JOHN LAKE (WC - 67)

Date Collected: 11 August 1966   Location: 5 m of Water, Center of lake

Sect. No.	Depth of Sediment (cm)	% Solids	Org-C	P	Fe	Mn	Ca	Mg	K	Al
			mg/g							
1	0- 5	3.10	232	4.23	59.3	1.03	2.10	3.40	4.44	18.8
2	5-10	3.54	240	4.26	57.9	0.903	1.76	3.01	4.10	19.9
3	10-15	3.85	260	4.08	49.7	0.820	1.76	3.28	4.30	21.5
4	15-20	3.51	268	3.89	41.5	0.744	2.08	3.59	5.05	24.2
5	20-25	4.20	268	3.12	38.6	0.656	2.73	3.73	5.26	24.9
6	25-30	4.46	296	2.44	40.5	0.570	2.72	3.94	5.30	23.6
7	30-35	3.87	334	2.00	37.1	0.512	3.28	4.55	5.56	22.6
8	35-40	3.96	345	1.99	44.3	0.500	3.18	3.95	4.96	21.1
9	40-45	4.19	367	2.21	34.9	0.496	3.25	3.95	4.74	21.0
10	45-50	4.09	364	1.66	35.3	0.484	3.41	3.79	4.40	22.3
11	50-55	3.71	364	1.64	28.6	0.445	2.98	4.10	4.36	22.7
12	55-60	3.74	349	1.79	36.4	0.450	3.27	4.59	5.29	24.2
13	60-65	4.10	351	1.71	34.9	0.439	2.78	4.14	5.21	23.2
15	70-75	5.70	326	1.52	40.1	0.432	3.14	4.58	5.63	27.6
16	75-80	5.23	310	1.52	32.8	0.432	3.63	4.25	5.36	27.4
17	80-85	5.28	320	1.50	38.1	0.457	2.92	4.42	5.98	—
18	85-90	4.75	309	2.03	42.6	0.522	2.67	4.03	--	27.2
19	90-95	4.52	306	1.68	35.9	0.454	2.84	4.32	5.52	29.3
21	100-105	5.32	334	1.47	32.0	0.430	3.03	4.31	5.53	29.1
23	110-115	5.60	353	1.52	34.5	0.470	2.96	4.14	5.36	24.3
25	120-125	6.51	338	1.35	25.5	0.441	2.90	4.29	5.44	21.2
27	130-135	5.81	346	1.19	21.0	0.369	2.57	3.88	5.28	24.4
29	140-145	6.01	320	1.02	12.4	0.368	2.84	4.18	5.82	23.5
31	150-155	6.13	269	0.920	14.4	0.304	2.39	3.57	5.51	23.8
33	160-165	6.17	255	1.17	14.8	0.282	2.34	3.48	5.84	25.7
35	170-175	7.00	287	1.14	11.7	0.305	1.77	3.19	5.55	24.7
Mean Density		1.03								
Standard Deviation			$^{5}6.6$	$^{36}0.032$	$^{36}1.7$	$^{36}0.0024$	$^{36}0.072$	$^{36}0.077$	$^{36}0.17$	$^{36}2.8$
Standard Deviation			$^{25}5.5$							

LITTLE ST. GERMAIN (L - 73)

Date Collected: 1967   Location: 3.1 m of Water, South Bay

Section No.	Depth of Sediment (cm)	% Solids	Org-C	P	Fe	Mn	Ca	Mg	K	Al
			mg/g							
67	0-13	2.26	385	1.25	13.2	0.175	1.55	2.15	2.65	10.6
66	13-25	1.99	391	1.16	13.1	0.170	1.55	2.08	2.69	11.3
65	25-38	2.06	382	1.13	13.9	0.176	1.62	2.11	2.90	11.3
63	51-64	2.31	357	1.12	16.4	0.192	1.63	2.48	3.57	12.3
62	64-76	2.68	350	1.13	18.5	0.218	1.38	2.82	4.25	15.2
61	76-89	2.66	368	1.16	17.1	0.212	1.40	2.35	3.78	12.8
60	89-102	2.95	382	1.18	17.0	0.221	1.03	2.27	3.54	19.3
59	102-114	3.12	335	1.06	13.7	0.224	1.16	2.17	3.35	16.2
58	114-127	2.95	334	1.06	14.4	0.224	1.34	1.78	2.70	13.5
57	127-140	3.19	351	1.06	14.6	0.238	1.51	2.00	2.65	14.7
56	140-152	3.28	344	1.07	13.7	0.258	2.00	1.67	2.59	13.3
55	152-165	3.36	344	1.05	16.4	0.262	1.50	1.85	2.59	13.5
53	178-191	3.22	356	0.914	13.5	0.251	1.65	1.50	2.56	13.0
52	191-203	3.74	358	1.05	15.6	0.260	1.61	1.99	3.40	15.7
51	203-216	3.45	361	0.935	12.2	0.252	1.91	1.57	2.16	12.2
48	241-254	3.57	359	1.02	—	0.244	2.13	1.61	2.08	10.5
45	279-292	3.75	356	1.04	12.5	0.244	1.66	1.77	2.18	15.8
42	318-330	4.45	340	1.06	15.3	0.270	1.19	2.20	2.78	10.5
39	356-368	4.60	364	1.07	15.6	0.299	1.42	1.95	2.82	13.1
36	394-406	5.61	331	0.945	14.1	0.318	1.47	2.85	3.79	23.1
33	432-445	6.20	304	1.01	15.1	0.321	1.42	3.28	5.44	17.3
30	470-483	6.37	315	0.935	13.1	0.336	1.46	2.56	3.78	20.5
27	508-521	7.60	282	0.906	15.6	0.340	1.63	3.16	4.76	20.3
24	546-559	8.56	282	0.870	14.1	0.314	1.46	3.09	4.76	20.2
22	572-584	7.90	314	0.895	15.9	0.326	1.47	2.90	4.92	21.8
20	597-610	8.52	306	0.805	13.1	0.335	1.45	2.99	5.33	22.5
18	622-635	10.3	270	0.785	14.4	0.333	1.66	3.21	6.28	29.2
16	648-660	11.3	248	0.755	12.8	0.351	2.30	3.52	6.24	29.9
15	660-673	10.9	268	0.795	13.5	0.336	2.26	3.66	6.66	28.9
12	699-711	14.6	223	0.846	17.3	0.327	2.43	4.24	8.45	32.5
11	711-724	17.9	215	0.790	15.6	0.309	2.85	4.45	10.6	39.9
Mean Density		1.02								
Standard Deviation			$^{31}8.3$ $^{15}7.7$	$^{11}0.01$	$^{11}0.28$	$^{11}0.0033$	$^{11}0.23$	$^{11}0.24$	$^{11}0.38$	$^{11}0.67$

APPENDIX B

Mathematical Formulae Utilized During Investigation:

1. Standard Deviation

$$\sigma = \sqrt{\frac{\Sigma(X_i - \bar{X})^2}{N-1}}$$

2. Relative Standard Error

$$e = \frac{\sigma}{\bar{X}}$$

3. Linear Correlation Coefficient

$$r = \frac{N\Sigma XY - \Sigma XY}{\sqrt{N\Sigma X^2 - (\Sigma X)^2} \cdot \sqrt{N\Sigma Y^2 - (\Sigma Y)^2}}$$

4. Significance Level of Correlation based on "t" tables from the equation

$$t = \sqrt{\frac{r^2(N-2)}{1-r^2}}$$

5. Standard Error of Estimate

$$s = \sqrt{\Sigma Y^2 - (a\Sigma Y + b\Sigma XY)}$$

σ = standard deviation

e = relative standard error

r = linear correlation coefficient

t = significance level of correlation

s = standard error of estimate

a = Y intercept

b = slope

X,Y = variables

N = number of observations

1 Accession Number	2 Subject Field & Group 02K	**SELECTED WATER RESOURCES ABSTRACTS** INPUT TRANSACTION FORM

5 Organization

Wisconsin Univ, Madison, Water Resources Center, Water Chemistry Laboratory

6 Title

CHEMICAL INVESTIGATION OF RECENT LAKE SEDIMENTS FROM WISCONSIN LAKES AND THEIR INTERPRETATION,

10 Author(s)

Bortleson, Gilbert C

16 Project Designation

16010 EHR

21 Note

22 Citation

Thesis submitted to the Graduate School of the University of Wisconsin, Madison, in partial fulfillment of the degree of Doctor of Philosophy, August 1970.

23 Descriptors (Starred First)

*Sediments, *Lakes, *Chemical analysis, Stratigraphy, Cores, Lake soils, Evaluation, Sedimentary petrology, Wisconsin, Eutrophication, Chemical stratification, Nutrients, Inorganic compounds, Nitrogen, Phosphorus, Carbon, Calcium, Magnesium, Potassium, Aluminum, Iron, Manganese

25 Identifiers (Starred First)

*Calcareous lakes, *Noncalcareous lakes, Lake Mendota (Wis), Madison lakes (Wis), Post cultural lake sediments, Precultural lake sediments, Organic carbon

27 Abstract

To trace the effects of cultural eutrophication, one meter sediment cores were used to determine the history of calcareous and noncalcareous Wisconsin lakes. Cores were analyzed for carbon, phosphorus, calcium, magnesium, potassium, aluminum, iron, and manganese. Determination of organic nitrogen, exchangeable ammonium and acid soluble phosphorus were made on selected sedimentary profiles. Recent sedimentation rates and identification of pre- and postcultural sediments were determined by ragweed pollen. Enrichment of phosphorus in postcultural Lake Mendota (Wis) sediments is not only the effect of increased phosphorus supply from domestic sewage but also due to increase in phosphorus retentive capacity of postcultural sediment and increase of phosphorus deposition due to concomitant increase of iron, manganese, potassium, and aluminum-containing compounds. Evidence indicates long, stable, conditions existed in this lake and watershed prior to human habitation, when phosphorus deposition rate multiplied 5-8 times over the precultural interval. Phosphorus concentration is largely controlled by iron and to a lesser extent by manganese deposition. Chemical stratigraphy of concentration-depth diagrams permit a qualitative evaluation of cultural activities. Potentialities and limitations of using recent lake sediments to evaluate eutrophication are discussed. (Auen-Wisconsin)

Abstractor V. S. Auen	Institution Wisconsin Univ, Madison

WR 102 (REV JULY 1969)
WRSIC

SEND TO: WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U S DEPARTMENT OF THE INTERIOR
WASHINGTON, D C 20240

☆U.S. GOVERNMENT PRINTING OFFICE: 1972 484-482/32 1-3